

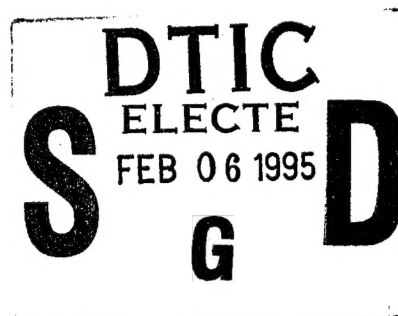


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# Nanoscience and Nanotechnology in Europe

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*Associate Director of Research for Strategic Planning*



December 30, 1994

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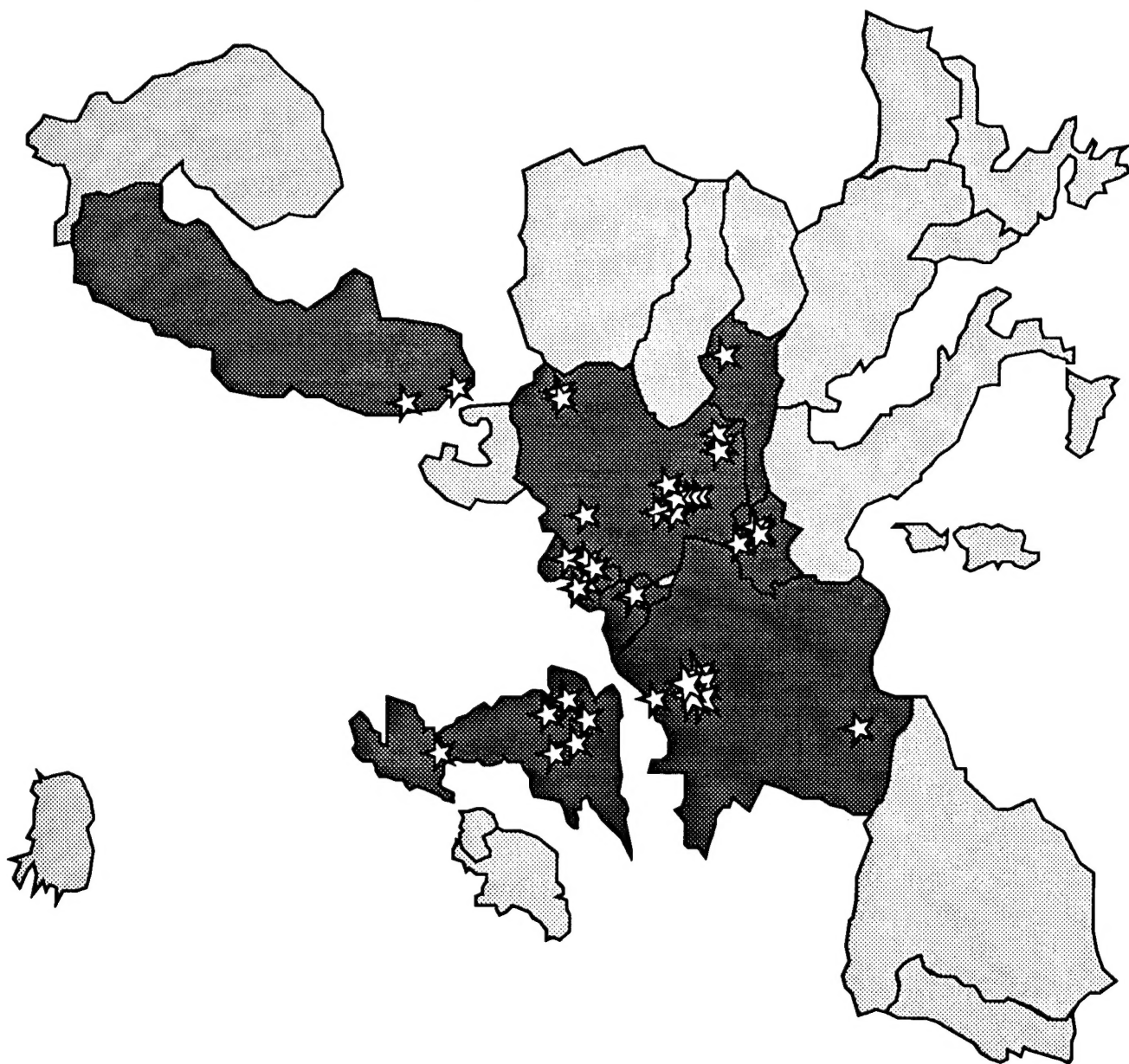
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**SITES OF EUROPEAN  
LABORATORIES VISITED  
25 March - 16 September 1994**



## **PREFACE**

During six months from April to September, 1994, I visited 42 laboratories in eight different European countries involved with research in nanostructures. The subject of nanostructures is currently a rapidly advancing frontier with considerable interest scientifically as well as technologically. The potential utilization of the fruits of this research for applications in information technology, sensors, and new materials, replete with the implications for an enhanced defense posture, places this research as a priority area to understand. It is a suitable topic for the recently introduced "focused technical assessment" activities of the Office of Naval Research Europe where I was located for the six-month period. This examination of nanoscience/nanotechnology was supported by the Office of Naval Research and the Naval Research Laboratory. Multidisciplinary efforts in fields of physics, electrical engineering, materials, chemistry, and biology are presented.

### **Focus of Efforts**

The focus of the effort was to view those rapidly advancing scientific frontiers (and technological consequences) associated with fabrication, characterization, and utilization of very small material structures. This included efforts by the more traditional electronics and semiconductor communities to prepare smaller features in semiconductors, by the optics community to prepare quantum dots and wires, by the local probes community to design new instrumentation and obtain amazingly detailed features with resolution approximating one angstrom, and by the chemical and biological communities for their methods of "self-assembly" for fabricating structures larger than single molecules. The innovation occurring in these overlapping fields is remarkable, with a vibrant and intellectually stimulating community discovering new methods to fabricate matter and to examine features not observed (or even expected) before.

### **Thin Films**

The field of heterojunction semiconductors has been a rapidly advancing materials frontier for more than a decade. This field continues to discover new phenomena, but is well understood relative to that involving nanostructures confined by at least one more dimension (i.e., quantum wires and quantum dots). On the other hand, thin films of organic materials are poorly understood, and have had considerable interest within the past decade. It is for this reason that the subject of organic thin films was included in the examination of nano in this exercise, but heterojunction materials were not made a specific focus for the visits scheduled.

### **Strength of Materials**

The field involving the strength of materials having nanodimensional crystallite sizes was not examined during this exercise. Initial attempts to contact key members of this field in Europe were unsuccessful. This particular community does not seem to overlap with those rapidly advancing frontiers made possible by the semiconductor community, the local probes community, or the self-assembly/supramolecular interactions community (all of whom are interacting in a fascinating, multidisciplinary, and synergistic manner).

### **Magnetic Effects**

Magnetic effects of nanostructures were encountered during several visits, however it was not made a specific focus of the visits. The field involving magnetic properties of matter is vast and rapidly advancing on its own frontiers. Some of the advances are due to the properties of thin nanodimensional films, and quite properly could be included in this field. Limited time, however, did not allow more complete coverage here.

## Superconductivity

The superconducting community has begun to focus attention on nanostructures. Effects that have been studied for several years involving boundary conditions, interference, etc. with semiconductors also take place with Cooper pairs in superconductors. The coherence length of charge carriers in superconducting metals is approximately that of high-mobility charge carriers in semiconductors. Thus, many of the effects examined by the semiconductor community offer new opportunities for observing superconductor behavior. This was evident only after visiting a number of laboratories in Europe, with pertinent comments included in this report.

## Acknowledgment

A large number of individuals cooperated to make this effort productive and stimulating. Included are the Deputy Chief of Naval Research, Fred Saalfeld; the Director of Research at NRL, Dr. Timothy Coffey; the Commanding officer at ONR-Europe, CDR Dale Milton; and the Chief Scientist at ONR-Europe, Dr. John Silva. Thanks are offered to many scientists in the U.S. for suggesting contacts in Europe for this exercise: Ari Aviram, Nick Bottka, Jeff Calvert, Rich Colton, Dave Ferry, Hal Guard, Wiley Kirk, Christie Marrian, Tom McGill, Jim Murday, Harvey Nathan, Marty Peckerar, Mark Reed, Joel Schnur, Gerry Sollner, Jim Tour, and George Whitesides. Last, and most importantly, is a long list of researchers in Europe who accepted requests to visit their laboratories, and who cooperated to make these visits most stimulating. Due to the limited time available to visit the laboratories in Europe, a number of excellent research establishments were not visited. I offer all due apologies to those who were not included in my itinerary; perhaps on another occasion the spectrum of contacts involving the excellent European research in this field can be broadened.

This information, including appendixes, should provide a convenient reference for researchers in the field. It is hoped that interactions, new ideas, and a stimulation of research in the field may take place through the efforts documented here.

*William M. Tolles*  
*Naval Research Laboratory*



## 1. INTRODUCTION

Nanoscience/nanotechnology (referred to henceforth simply as "nano") is the science of fabricating, characterizing, and utilizing structures having dimensions of approximately 1 to 100 nanometers. Various perspectives make the meaning of the term nano somewhat ill-defined: it involves structures smaller than those currently in production or considered for near-term production of microelectronics; it involves structures in which confinement effects due to boundary conditions make matter behave differently than that of bulk matter; it involves molecular structures larger than 1 nm; or, it involves thin films having submicron dimensions, a field of current interest. The selection of information obtained with the visits to European laboratories encompasses an admixture of these definitions that could be assembled and followed in a limited six-month period.

### 1.1 Organization of this Document

**Fabrication** methods represent the basis for the entire field of nano. **Characterization** techniques have been advancing quite rapidly with the introduction of local probes in the early 1980s. **Utilization** of the information obtained in these research frontiers is becoming diverse and more frequent. Each of these perspectives is deserving of a separate chapter, even though utilization necessarily involves fabrication and characterization. Community interactions currently advancing capabilities, however, are more frequently associated with a focus on either fabrication or characterization. A number of efforts are beginning to include a combination of categories such as fabrication and characterization. Programs with these combined efforts are included in the activity taking place at a latter stage in the program (e.g., fabrication and characterization efforts combined would be found in the characterization section). Information about the laboratories visited and the individuals mainly responsible for them is found in Appendix A.

### 1.2 Research Management Perspective

Inevitably, in discussing research interests with scientists, subjects of conversation tend to broaden into areas very much on the mind of each individual, such as research management perspectives, interactions of particular value, and the health of the community. Many of these comments are very informative, and are introduced as a research management perspective in Appendix B. It is hoped that management perspective will be obtained from this appendix as well as the technical content contained in the body of this report.

## 2. FABRICATION

The methods of nanostructure fabrication are fundamental to the entire field of nanoscience/nanotechnology. If there were good ways to fabricate precision features of semiconducting material with feature sizes of 10 to 100 nm for chips in a massively parallel mode, such methods would most likely be in use commercially. The limiting performance (information density, speed, storage capacity, etc.) depends critically upon extremely reliable rapid fabrication methods. Optical lithography is the current commercial method of choice. Alternatives to optical lithography as feature sizes become smaller (less than 0.2  $\mu\text{m}$ ) are under intense examination with noticeable differences of opinion about the best approach.

### 2.1 Lithography

Lithography is the key to producing electronic chips today. It is exceptionally important that this field be understood and exploited to the fullest, as it represents the frontier for the hardware used in information technology. It is likewise necessary to recognize that industrial production of micro- or nanostructures requires rapid and reproducible patterning with feature sizes as small as is reasonably possible (with rates on the order of  $10^{12}$  pixels/wafer exposure). Parallel techniques of fabricating nanostructures thus are of considerable interest for possible industrial application, whereas serial techniques are important for fabricating laboratory structures for research purposes or for initial fabrication of lithographic masks.

Some reserved viewpoints were expressed by some European scientists about lithography research and the minimal progress that has been made over the last 10 years in this field. The ability to prepare patterns with 10 nm resolution was evident a decade ago. The fabrication method for this, however, is the use of a focused electron beam; a serial method is able to fabricate features with limited speed (1 GHz is about the upper limit) and is not able to economically compete with parallel methods involving radiation and masks. Little progress has really been made since then in spite of significant effort in this area. With fabrication tools at their disposal, several groups are able to prepare structures with 1.2 nm lateral resolution. The major question is: what will be done with them if they are fabricated?

#### 2.1.1 Large Scale Parallel Fabrication Lithography

The excellent resolution offered by electron beam lithography, along with the high degree of flexibility found in the basic design, suggests the possibility that such an instrument may be the next generation exposure tool for mass production of chips. The ability has been developed to obtain 100,000 lines per field with a good image projection capability for electron beams. Along with the ability to "stitch" multiple images with suitable distortion compensation at each mask, exposure of large wafers with electron beams in a reasonable time scale is becoming a reality with electron beams [1]. By using multiple printing of Moire patterns, small levels of distortion may be detected (within three parts in  $10^4$  of grating pitch) [2]. Computer processing of image information is far more sophisticated now than several years ago; automatic detection and compensation for distortion effects is far easier.

With electron lithography, it is becoming clear that the performance of the resist along with the need to avoid shot noise are becoming the limit. A resist such as SAL 601 has an inherent resolution limit of 30 nm due to the size of the molecular change that takes place upon exposure and development. Further, this limit is obtained with about 100 electrons, which results in a 10 percent fluctuation in intensity over a pixel this size. This fluctuation is inherent in the statistical variation of that many electrons. If smaller pixel sizes are required, less sensitive resists must be incorporated along with greater exposure levels.

With the above developments, it is clear that the electron beam community is out to win over some very important advocates: the industrial interests for large-scale production of chips. The advantages of this form of

lithography were not understood several years ago when decisions were made to support competing technologies. Now that these advantages are becoming clear, this community feels it is time to make decisions supporting the appropriate developments in electron lithography for this purpose.

### 2.1.2 Lateral Patterning

A group at Cavendish Laboratory, Cambridge is using a modified 100 keV Scanning Transmission Electron Microscope (STEM) in order to get electron beams with a diameter of approximately 2.5 Å from a cold emission source. This beam may be scanned over a distance of a micron or two. Patterning of  $\text{CaF}_2$ ,  $\text{SrF}_2$ , and  $\text{Ca}_x\text{Sr}_{1-x}\text{F}_2$  materials is being investigated. The mixed calcium/strontium salt has an advantage that it may be prepared with lattice parameters matching those of GaAs. The group at Cavendish Laboratory is able to grow 1-2 nm holes in this salt. A major problem does exist with such materials in that GaAs is grown at 600° C. When the material is cooled, due to a substantially different coefficient of expansion, the salt does not adhere very well to the GaAs.

Cavendish Laboratory is also looking at the fabrication and characterization of quantum wires by heterojunction growth on obliquely cleaved heterojunction structures. If subsequent heterojunction growth takes place across these intersections, any applied voltage to the original heterojunction material will serve to deplete rows within the second heterojunction material, forming in effect parallel quantum wires in the second heterojunction material. Experiments are under way to characterize these materials.

#### 2.1.2.1 X-Ray Lithography

The Laboratoire de Microstructures et de Microelectronique in Bagneux, France has had considerable experience with X-ray lithography using as an X-ray source the synchrotron located in Paris-Sud University (Orsay). The masks consist of tungsten on silicon carbide membranes. Patterns with 50 nm resolution on 30 mm samples are routinely produced, and alignment is not a problem with overlay of successive exposures using a Karl Zeuss stepper having 10 nm position accuracy and 40 nm precision. The radiation source at Orsay (Ring SuperACO at LURE Laboratory, U. Paris-Sud) currently requires a one minute exposure time using PMMA with 0.7 nm × rays (center wave length). Future research envisions combining improvements such as phase contrast methods, effects due to multiple wavelength exposure, wave guide effects, and understanding effects due to silicon carbide. For example, although the optimal thickness of tungsten masks was originally thought to be 700 nm, by examining in detail interactions with many of the effects mentioned above, it is found to be only 300 nm. By understanding and optimizing all of these effects simultaneously, considerable improvement in resolution is envisioned. A goal of researchers at Bagneux is to demonstrate 10 nm resolution, and they expect that it will be readily obtained in the next two years. Some sources are also available in Grenoble for future research.

#### 2.1.2.2 Ion Beam Lithography

Fabrication of nanostructures using ion projection beam lithography has been a specialized research area for a number of years [3, 4]. Two ion beam instruments have been designed and built in conjunction with Ion Microfabrication Systems (IMS) in Vienna: one is located there and the second is at the Fraunhofer Institute in Berlin. A third instrument is being designed (and, again, partially constructed) by IMS to be located in the U.S. under the support of the Advanced Lithography Group (ALG) in the U.S. The instrument to be shipped to the U.S. will have a capability of exposing areas of 20 mm × 20 mm with 180 nm resolution in a 0.5 second exposure time. This is done with a 3:1 demagnification ratio projecting ions through an "open stencil mask" (this mask requires multiple exposure in order to close gaps necessary to keep the stencil together mechanically). The hydrogen ion or helium ion beam is accelerated from approximately 10 keV to a higher voltage for deposition and exposure of resists (55 keV at Vienna, 70-80 keV at Berlin, and 150 keV for the ALG instrument).

One significant change in the operation of the Vienna machine within the last year is the introduction of proximity exposure, a technique that appears to give good results.

A number of images were shown having feature sizes well within  $0.15\text{ }\mu\text{m}$ , with frequent occurrence of  $0.1\text{ }\mu\text{m}$  and even one exposure with  $0.07\text{ }\mu\text{m}$ . It is not always clear which of these images was fabricated with 10:1 reduction methods and which used the newer 5:1 method (the 5:1 method gives, of course, larger sizes over a larger field).

No multiple beam exposures have been attempted with these machines, as they are experimental and for the purpose of demonstrating the limits of the methodology. Applicable devices that have been fabricated with these machines include electrodes for surface acoustic wave (SAW) devices and quantum dots.

IMS continues to examine ways to minimize the aberrations due to spherical electrostatic focusing fields and dispersion of a polychromatic beam due to the initial spread in ion speeds in the plasma source [5-8]. Unfortunately the optimum conditions to minimize one form of aberration are not the same as those to minimize the other.

Mask and image placement for multiple exposure has been considered for these machines, and is facilitated by the ability to electrostatically move the beam image while focusing on fiducial marks. It is estimated that image placement can be controlled (with active feedback) to approximately  $20\text{ nm}$ .

The period during the last few years has seen a factor of 40 improvement over the capabilities demonstrated with the current machine through refinements in design. Further enhancements are foreseen through improvements in electrostatic lens design. Overall, IMS believes that with future developments it will be possible to obtain  $20\text{ nm}$  feature sizes over a  $6\text{ mm} \times 6\text{ mm}$  field with 10:1 projection techniques.

Resists that work well with ion beam exposure were developed to demonstrate the effectiveness of feature definition with ion beams [9, 10]. Within the last few years was recognized that the usual novolak-based resists were not useful for fabricating structures below  $0.3\text{ }\mu\text{m}$  [11, 12]. Polyimides offer opportunities for resists as they form hard polymers with minimal ion beam exposure. It is found that  $0.2\text{ }\mu\text{m}$  of resist is sufficient to withstand reactive ion etching. Exposure levels required approximately one microcoulomb/cm<sup>2</sup> (dictated by shot noise requirements).

### 2.1.3 Etching Mechanisms and Characterization

Some of the intricacies of etching behavior have been carefully and productively examined at Glasgow. One effect, referred to as "side wall etching," has become understood in more depth [13]. In this phenomenon, directional etching of structures that have high aspect ratios is not as good as theoretically possible because of attractive forces between a passing ion and the wall. It is simple physics to understand the presence of a countercharge image as an ion passes a conducting wall (the field at the surface of a conductor must go to zero). This countercharge is an attractive force that causes unidirectional ion etching to undercut vertical walls and give decreased overall performance of intended nanostructures.

Some beautiful experiments were described in which the depth of damage in an ion etched surface was measured. This was done by measuring the conductance of a geometric structure as a function of the width of the structure [14]. The conductance will extrapolate to nearly zero at zero width if the structure has no damage (it does not extrapolate exactly to zero due to side wall effects in the relaxation of the charge carriers). For different etching conditions, this same plot produces a functional dependence parallel to that of an undamaged structure. By noting the width at zero conductance, the width of the damaged surface is determined.

Using this tool, selected etching conditions can have less than 2 nm depth of damage, or as much as 20 nm [15, 16]. The conditions for minimizing damage are set down in these studies. Electron cyclotron resonance (ECR) tends to damage surfaces excessively (it is  $\text{Cl}^-$  that does the damage). Magnetically confined plasma etching seems to produce relatively smooth surfaces. At power levels of less than 15 W, low damage occurs since the principal constituent is the chlorine molecule rather than the chloride ion. The chloride ion produces surface damage and resulting depletion; a "mushy" surface is also the result of chloride ion etching. Consequently, less damage results at these low powers. It seems that methane/hydrogen gas is a useful "universal etch" for II-VI materials [17].

#### 2.1.4 Mechanisms Involving $\text{Ca}_x\text{Sr}_{1-x}\text{F}_2$

The surface modification portion of a program at Cavendish Laboratory, Cambridge is examining mechanisms of electron beam lithography. A current system of interest is the etching of calcium/strontium fluoride. Damaged fragments are observed by mass spectrometry. Positive fluoride ions have been observed to emerge with a 24 eV threshold. The mechanism for this emission appears to be an interatomic Auger decay process.

A rather sharp peak has been observed for the dissociation cross-section of the oxygen molecule to its atoms at approximately 8 eV. The products of this dissociation excited by electrons are oxygen atoms and singly negative oxygen ions. The cross-section above 8 eV is reduced dramatically to about 17 eV where the products are positive and negative ions. Future research in this area involves the role of low energy electrons and how they may be controlled. Also future research involves the use of scanning tunneling microscopy (STM) techniques with surface models. Several STM units are being installed at Cavendish Laboratory where the role of low energy electrons in lithographic processes and new fabrication schemes involving STM will be investigated.

#### 2.1.5 Proximity Effect Reduction

Enhanced resolution of lithographic methods is always of interest; substantial improvements have been reported recently at Cavendish Laboratory, Cambridge. The proximity effect limiting resolution of electron beam lithography due to scattered electrons has been given some attention quite productively. Instead of focusing attention on improving the exposure aspect of the problem and attempting to vary the degree of backscatter from electrons, an alternative approach modifies the development procedure. At dimensions of 10 nm or below, the surface forces holding matter together (e.g., van der Waals and other forces) become very high. This limits the lift-off processes commonly used to obtain contrast between exposed and unexposed regions of an image. Reasoning that this is the case, a group in Cavendish Laboratory investigated the development process in the presence of ultrasonic agitation. Variations in the exposure levels and in the level of ultrasonic agitation were examined. With this alternative method, a substantial decrease in feature dimensions is observed [18, 19]. It is now possible to obtain 5 nm lines with this technique, and it is hoped that additional experimentation will demonstrate 2 to 3 nm widths.

Electron beam exposure tools are available at Cavendish Laboratory with beam sizes on the order of 3 nm with 100 keV electrons. With the fine lithographic tools available, a group at Cavendish Laboratory has made a variety of multiple tunnel junction devices with delta-doped GaAs/AlGaAs and has investigated the side-gating technique to squeeze the channel dimensions with the familiar depletion effects [20]. At temperatures of 4 K, they have made a memory involving 10 electrons using these devices. The limits of these coulomb blockade devices continue to be examined and understood.

### 2.1.6 Patterning with Local Probes

The use of local probes for patterning nanostructures on surfaces is under widespread investigation. Just what the limits are for these techniques is not well understood, and this appears to be an important scientific question. Local probes may be a relatively inexpensive way to fabricate structures that, previously, were mainly obtained by high-voltage electron lithographic methods. These structures are likely to be most useful in laboratory experiments rather than for any commercial fabrication due to the low production rate relative to that required for commercial purposes.

#### 2.1.6.1 Patterns in Thin Metal Films; Silicon Structures with Tunneling Tips

Electrical noise patterns in thin wires are modified by boundary conditions. The desire to measure these effects is an incentive for introducing new methods of patterning metal film structures at Philips Laboratory, Eindhoven. The shot noise in such thin wires is supposed to be reduced (by 33 percent) by quantum interference effects. One condition for this to be true is that the inelastic scattering length should be longer than the length of the wire. The scattering length at the Fermi level for metals is 10 to 20 nm at room temperature and approaches one micron at low temperatures. Additionally, ferromagnetic wires are of interest. The noise properties in tunneling tips represents another area of interest.

The emerging technique of writing on passive silicon with tunneling tips has been used at Philips Laboratory, in addition to several other laboratories now working with this technique. The resolution achieved allows 20 nm lines to be written, similar to observations elsewhere. One additional feature in the research done here is that such patterns have been successfully written on amorphous silicon—this works on 20 to 50 nm-thick silicon. This process is now being used to deposit silicon on metals and subsequently write on the silicon to transfer the patterns to the underlying metals. The process consists of a wet etch to remove the silicon that has not been exposed to the tip, followed by a dry etch to pattern the metals.

The difficulty of making 10 nm thick metal films due to the finite metal grain size has been encountered at Philips Laboratory (as in other laboratories). Deposition using magnetron sputtering seems to reduce grain size. Further, diode/triode sputtering that incorporates argon ions having a few hundred electron volt energies seems to successfully give thin metal films. A correlation has been found between the melting point of the metal and grain size (higher melting points give smaller grain sizes). Diode-sputtering of a tantalum-iridium alloy gives a metal film 10 nm thick with a roughness of less than 1 nm.

#### 2.1.6.2 Fabrication of Gold Nanostructures with Local Probes

A Nanoscope II STM unit has been modified at Katholieke Universiteit, Leuven, Belgium to write patterns using electron exposure from the scanning tip. Pressures of nitrogen of about 10 mtorr have been introduced in the sample chamber to permit this, and an electronic board has been introduced to allow vector positioning of the tip. "Resist" materials have included omega-tricosenoic acid [ $\text{CH}_2=\text{CH}(\text{CH}_2)_{19}\text{CO}_2\text{H}$ ]. This molecule, when exposed to an electron beam, polymerizes at the  $-\text{CH}=\text{CH}_2$  group. This polymeric film, when formed with four layers of a Langmuir Blodgett film, is sufficient to protect a 25 nm layer of gold with Argon ion etching. This approach is used to write 20 nm-wide lines of gold 25 nm deep (15 nm have been written, but not reproducibly at the lowest resolution obtained) [21, 22].

## 2.2 Methods of Heterojunction Fabrication

The basic optical properties of heterojunction materials have been reviewed [23-25] for application to electronics and optics. This is a fundamental capability that makes many of the fabrication techniques with nanostructures possible.



### 2.2.1 MBE-Atomic Beam Instrumentation

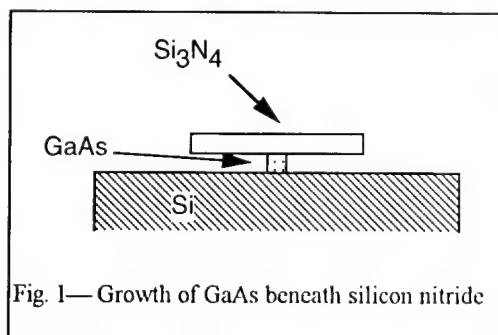
A unique instrument has been constructed at Philips Laboratory, Eindhoven (over the last seven years) for specialized MBE/ion beam deposition of materials. The impetus for the construction of this instrument comes from the difficulties of preparing materials with a high-density of doping in semiconductors. Frequently, when high levels of dopants are introduced and annealed, the dopants will precipitate, leaving poorly defined or poor grade materials. Alternatively, when MBE chambers are used for high levels of dopants, they become contaminated and the dopant appears in just about any future attempts to use the chamber.

Thus the unique design of this instrument has been introduced. It has a number of chambers for MBE deposition and in situ analysis, similar to those in many other laboratories. The important difference is the introduction of a 30 keV (initial voltage) beam of atoms such as phosphorus, arsenic, or boron. This is an unfocused ion beam that is able to implant ions while growing structures with the usual MBE processes. The beam passes through a voltage-controlled region to reduce the beam energy to the range of 200 eV to 3 keV. The dopants may be introduced uniformly (within 10 percent) on a six-inch wafer, and dopant levels of up to  $10^{21}/\text{cm}^3$  have been produced (with phosphorus, for example). A good deal of flexibility has been introduced with the completion of this fabrication instrument.

Silicon-germanium heterostructures are of interest at Philips (as in a number of laboratories) for their ability to potentially integrate with silicon processes for commercial chip production. One goal is to produce 150 GHz heterojunction bipolar transistors. Another is to produce thin (10 to 20 Å) layers of a p-n junction at a surface for efficient electron emission from surfaces. Mobilities of  $200,000 \text{ cm}^2/\text{V-s}$  have been observed in some silicon-germanium structures made elsewhere at a strained silicon edge (100 Å) with  $\text{Si}_{0.7}\text{Ge}_{0.3}$  on either side. A desired material is that of Si/Ge with four atomically smooth layers of each alternating section. Ideas such as this are being pursued to improve the performance of material properties associated with silicon/germanium.

### 2.2.2 Dislocation-free GaAs on Silicon

Growth of GaAs on Silicon heteroepitaxially is difficult due to the lattice mismatch. A different approach to obtaining good material is being introduced at Villeneuve, France, as illustrated in Fig. 1. A "poor" layer of GaAs is first grown on the Si surface. An overgrowth of silicon nitride in a strip is next formed. Etching and removal of the GaAs then takes place, with severe undercutting of the GaAs under the silicon nitride layer. This etching takes place almost completely, but a small "sliver" of a GaAs remains in the center of the silicon nitride strip. Upon regrowth of the GaAs by VPE, the GaAs under the silicon nitride serves to seed single crystal growth, resulting in a quality GaAs material that grows under the silicon nitride. Apparently in this configuration the dislocations are blocked. This material luminesces, and lasers can be made with this material.



### 2.3 Focused Ion Beam Deposition

Focused ion beam (FIB) deposition is undertaken at Cavendish Laboratory with locally built (or modified) instrumentation. One instrument works with Au-Si-Be sources and magnetic deflection to obtain selected atomic beams having a focused diameter of 50 nm at 170 to 180 keV and 1 to 10 nA current. A second instrument involves beams generated with gallium at 40 keV. Using these techniques, a method of fabricating T-gates has been formulated. Beryllium is implanted in PMMA at depths of

about  $0.5 \mu\text{m}$ . A subsequent electron beam exposes this same region to the full depth of the resist with a higher resolution, thus exposing the resist for the "stalk." These exposed regions are removed with a development

process, leaving a shaped crater for a subsequent metal exposure. The resulting T-gates have gate lengths of 0.22  $\mu\text{m}$ . These procedures have produced MESFETS with frequency performance of 94 GHz. A continuing program involves a pseudomorphic high electron mobility transistor (HEMT) (strained lattice); with this they expect to reach 144 MHz with 0.1  $\mu\text{m}$  T-gates.

Related programs involve the deposition of tungsten from tungsten hexacarbonyl. Exposure of the hexacarbonyl gas with electron beams decomposes the molecule with the consequent deposition of tungsten. The beam size in these experiments is approximately 0.02  $\mu\text{m}$ , and the resulting spot size is about 0.1  $\mu\text{m}$  in diameter. This work is in conjunction with Kernforschung Zentrum in Karlsruhe (KFK) in Germany for the purpose (at present) of repairing tungsten masks. One of the advantages of this method is that the deposition of the tungsten appears to be damage-free.

## 2.4 Nanostructures on Vicinal Surfaces

Single crystal structures cleaved or polished at angles slightly canted from that exactly exposing a single crystalline plane expose steps for each succeeding monolayer (terrace) of a vicinal surface. Growth of another material on a vicinal surface typically attracts the added material at the steps. In many cases this results in quantum wires consisting of diameters of only one atom and lengths of many atoms along each step. This has been demonstrated at the Laboratoire de Microstructures et de Microelectronique in Bagneux, France with AlAs on vicinal steps of GaAs when prepared at 520° C with less than a monolayer of AlAs on the surface. Polarization of the photoluminescent light has been observed, in accordance with expectations that electromagnetic emission will be anisotropic due to the anisotropy of the emitting quantum wire structure and the alignment of these wires all in one direction along the surface [26]. There was no dependence on the terrace length for the observed behavior. Future research along these lines will use vicinally sliced superlattice materials.

An interesting variation on this approach involves the growth of a two-dimensional electron gas (2-DEG) by fabricating a material step on a vicinal surface using a misoriented substrate. The result is a laterally modulated 2-DEG, with modulation periods of 8 to 30 nm. These materials should make interesting components or devices involving interference effects on charge carriers.

## 2.5 Molecular Self-Assembly

Molecular self-assembly uses the interactive forces of solid state lattice structures, chemical bonds, and van der Waals forces to form larger aggregates of atomic or molecular units with specific geometries. Research programs pursuing this approach are innovative and demonstrate the many approaches to fabricating nanostructures. Those skilled in the physical measurements of nanostructures are applying their instrument expertise to measure the various properties associated with these self-assembled systems. It is possible (and hoped) that certain properties will have surprisingly interesting utility. Molecular interactions that result in a specific attraction between neighboring molecules in specific orientations give rise to a wide variety of structures and specific chemical changes. The term "molecular recognition" refers to the phenomenon involving these interactions and the products (in many cases molecular aggregates) resulting from them. At the very least, such synthetic efforts demonstrate clever approaches to the design of a wide variety of nanostructures.

It is clear that this "bottoms up" approach can be used to make nanostructures that are identical to one another (a truly monodisperse sample size). This is in contrast to the samples made by, say lithography, that will inevitably show a degree of polydispersity due to the nature of statistical distribution of exposure (photons, electrons, or ions) and the statistical nature of causing a chemical change from exposing a molecular material. If the monodispersity of the "bottoms up" approach can be combined with the functionality and pattern definition of the "tops down" approach, it is conceivable that each may contribute to an even more interesting means of fabricating nanostructures in the future.

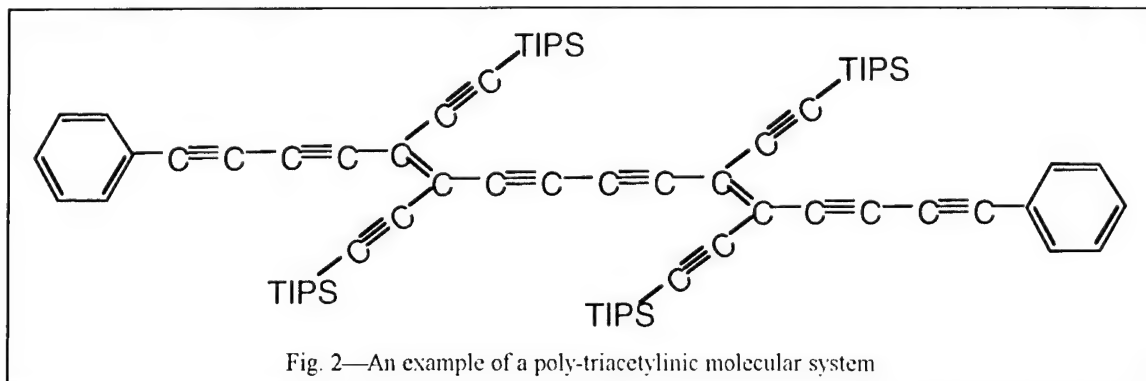


### 2.5.1 Dendrimers

Dendrimers are specific types of molecules grown by repetitive chemical reactions, each reaction of which adds a small number (two to six, nominally) of molecular fragments to the existing molecular framework. Each successive reaction thus leads to a molecule with an overall molecular weight of  $M^n$  where  $M$  is the molecular weight of the fragments added and  $n$  is the number of synthesis steps. By this method, quite large molecules have been synthesized at Eidgenoessische Technische Hochschule (ETH) Zurich (with molecular weights on the order of 19,000, or even more). These units that have been synthesized around a basic porphyrin unit are "beautifully soluble" even with the molecular weight of 19,000. Polymers, on the other hand, when synthesized by the usual polymer condensation routes, typically have a spread of molecular weights and are rather intractable for characterization due to the polydispersivity of these molecular weights.

### 2.5.2 Carbon Chemistry

Poly-triacetylenic materials have been synthesized with a great variety of molecular modification and properties [27]. These polymers feature a conjugated alternating single-triple bond in the polymer unit. Organic substituents may be placed along each monomer unit to give the resulting polymeric material a great deal of variability in its physical properties. Figure 2 shows an example of this material (TIPS is tri-isopropylsilane).



The basic material is not a good conductor of electricity, but it has a high nonlinear coefficient,  $2 \times 10^{-11}$  esu, comparable to polyacetylene, and it is paramagnetic. It is interesting to observe the oligomer units (small polymer chains having lengths of some 4 to 100 units) in conjunction with  $\text{UO}_2^{++}$ . The  $\text{UO}_2^{++}$  forms a complex with the oligomer unit at positions where the "R" groups branch from the main polymer chain (electrical neutrality is assured with additional ions present). The chain thus becomes a very heavy unit, with a sequence of  $\text{UO}_2^{++}$  units positioned along the chain. It is possible to observe the individual polymer chains with transmission electron microscopy (TEM) when these uranium dioxide ions are complexed with the chain.

Alternative conjugated materials have been formed from porphyrins (the basic unit is very similar to phthalocyanines). A rigid rod polymer of about 20 units (30 nm in length) has been synthesized with this material. The spectral characteristics indicate a shift of the energy levels toward the IR as the chain lengthens, similar to many other conjugated molecular systems.

A material consisting of 390 carbon atoms has been synthesized. The structure resembles a benzene ring, with  $\text{C}_{60}$  (fullerene) as a substituent at each of the six equivalent positions on the benzene ring. The linkage unit between the benzene ring and the fullerene structure accounts for the additional carbon atoms. Additional chemistry is being introduced in order to form tethered attachments from one position on the fullerene ring to a

specified carbon position several carbons atoms away [28, 29]. It is with such careful and clever synthesis that new nanostructures may be formed with well-characterized structures.

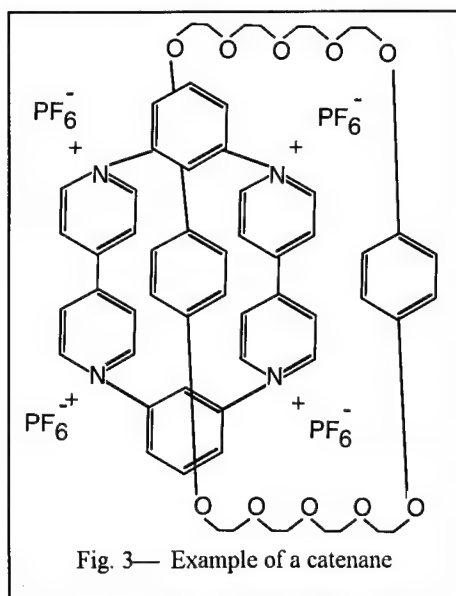
There is some effort at ETH, Zürich, in designing molecular systems that will be precursors to the fullerene sequence. This would presumably lead to a high yield of materials having the fullerene structure, something that could enhance the study of the field substantially.

### 2.5.3 Geometric Figures through Base Pair Manipulation

The base pairs of DNA have demonstrated how the various carefully placed amide linkages in a molecule may provide the attractive forces to form supramolecular structures through molecular interactions. DNA is the classical example. The base pairs found in nature are somewhat limited relative to the full spectrum of base pairs that can be designed by a synthetic chemist. One effort at ETH Zurich involves synthesizing a full complement of base pairs (including those not found in nature with DNA) and then forming clever geometrical shapes by reacting base pairs that bind selectively [30, 31]. Using this approach, molecular structures have been synthesized that have the shape of small boxes and other geometric figures. This represents an alternative means of building nanostructures using the "bottoms up" approach. A method has been developed here to predict the folded structure of these proteins, with remarkable accuracy for the predictions. Computer methods for analyzing massive amounts of protein sequence data were incorporated into the prediction models.

### 2.5.4 Catenanes

The catenanes are a group of molecules that are characterized by interlocking rings, where one ring molecule is formed such that it penetrates a second ring molecule (mechanical entanglement at a molecular level) [32]. Each ring consists of a sequence of aromatic rings or  $-\text{CH}_2-\text{O}-\text{CH}_2-$  groups. Ring sizes consist of as few as two benzene and two pyridine groups, or ten  $-\text{CH}_2-\text{O}-\text{CH}_2-$  groups with two benzene or pyridine groups, and as many as twenty  $-\text{CH}_2-\text{O}-\text{CH}_2-$  and four benzene or pyridine groups. Some of the original molecular systems represented by this class of molecules were made by Cram at UCLA. One of the smaller structures is represented in Fig. 3.



Simply the fabrication and characterization of these structures represent a fascinating new field of endeavor. Synthesis of these molecules involves a "self-assembly" process reminiscent of the self-assembly of viruses, where covalent and non-covalent associations are alternated to obtain the final product. The substituents on each ring give the various positions on the ring different characteristics (electrophilic or lyophilic nature, for example). Questions such as which positions of each ring are most often in contact, and in what proportion, are being revealed by this research. This type of information is most often revealed by NMR spectra, mass spectrometry, secondary ion mass spectrometry (SIMS), and X-ray diffraction. NMR spectra also reveal the rate of exchange between different conformations in the molecule.

The photochemistry and electrochemistry of these molecular systems have been examined. It is found that with electrochemical oxidation the change in electron distribution of the resulting product changes the ratio of the time each site on one ring associates with each on the other [33].

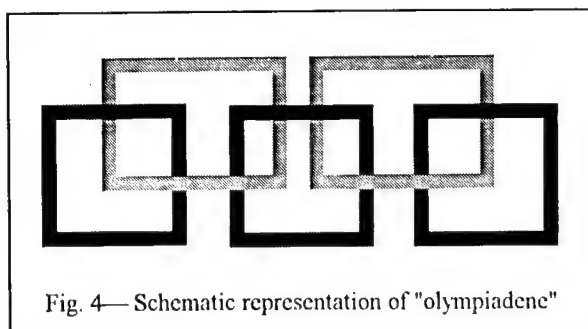


Fig. 4—Schematic representation of "olympiadane"

Besides the formation of two interlocking rings, molecules consisting of three and four interlocking rings have been fabricated and characterized. Additional structural complexity is associated with an increasing number of rings, as expected. The molecule with five interlocking rings has just about been synthesized; the name for it has been selected as "olympiadane" (after the geometry of the structure, of course), illustrated in Fig. 4. The ultimate of this sequence would be a polymer consisting of interlocking rings in a chain; the properties of such a

polymer would represent the characteristics of actual bond stretching and breaking of the interlocking rings (chains), a quite different approach to designing mechanical properties for polymers.

A number of these compounds have been reported in recent literature; there are many additional materials and studies continuing with these ideas.

### 2.5.5 Rotaxanes

The molecular structure represented by the general picture of a ring circling the central portion of a dumbbell, with the ends of the dumbbell (the "stopper") large enough to keep the ring from exiting the dumbbell, is known as a rotaxane [34]. The ring molecules resemble those used in the catenanes (above). The stopper groups are substituents such as tri-isopropyl-silyl. Such structures have been fabricated and characterized at the University of Birmingham, U.K. Operations for this fabrication include such terms as "clipping, threading, slipping, and stoppers."

Figure 5 shows a schematic representation of this structure; the ring molecule is represented in the middle, the "stopper" as a circle consisting of three isopropyl groups  $\{\text{iPr} \equiv [(\text{CH}_3)_2\text{CH-}]_3\}$  on silicon (Si), and different substituents along the center rod as "A" and "B."

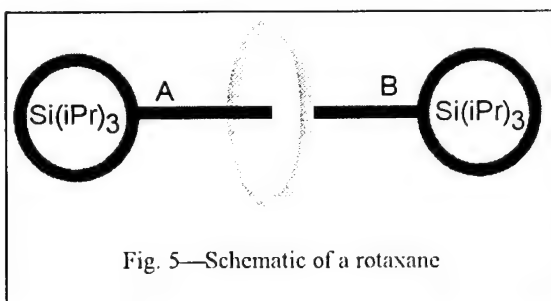


Fig. 5—Schematic of a rotaxane

The ring on this molecule can shuttle back and forth between the two ends, with a variation in the rate of transit as well as the amount of time spent on each. As with the catenanes, the association of the ring molecule with the end groups (or with substituents A and B in the middle rod) depends on the electrophilic and lyophilic nature of A and B with the ring. This changes with oxidation and the energy level of excited states. With oxidation and reduction, the basic unit thus becomes a

"memory unit," depending on the previous history of the molecule.

Under certain conditions, the photoexcitation, oxidation/ reduction, or protonation of rotaxanes can cause the ring molecule to change the preferred location from one side to another. This amounts to a mechanical motion of a molecular unit, and is envisioned as a possible source of mechanical energy at the molecular level. Such motions within biological molecules are found to be responsible for the contraction of muscle cells within living species.

### 2.5.6 Prediction/Modeling of Rotaxanes/Catenanes

The information about molecular conformations of rotaxanes and catenanes represent a wealth of information about molecular group interactions. Models to predict these conformations have been introduced, using electrostatic point charges estimated from semiempirical molecular orbital calculations. The dominant interactions involve hydrogen bonding and aromatic ring interactions. Mathematical models for minimizing the energy involve conjugate gradient techniques with a three-center force field involving charge-charge interactions. Inclusion of the hydrogen atoms is crucial in this process. Molecular clusters involving up to 800 atoms may be calculated with this approach using a Silicon Graphics workstation. Surprisingly good agreement is found between the experimentally determined molecular geometries and those predicted by the models [35]. The molecular complexes are essentially superimposable with structures obtained by X-ray diffraction data, predicting torsion angles and geometries quite well. This provides the ability to predict molecular geometries of systems prior to embarking on an experimental synthetic approach, an important ingredient for "materials by design."

### 2.5.7 Experiments with Quartz Balance

The use of the vibrating quartz crystal microbalance (QCM) for detecting small mass changes is used throughout a number of laboratories. A small mass change adhering to the vibrating quartz changes the resonant frequency; detection of this frequency shift is interpreted as a mass change; this change reveals considerable information about molecular interactions.

Research at Mainz, Germany, uses this approach. One molecular layer is formed at the surface of the QCM (this may be a layer of antibodies or antigens, for example). Attachments to the antibodies with antigens will be seen as a mass change. For a layer of streptavidin (a model molecular system) a frequency change in the quartz is seen to be  $70 (\pm 1)$  Hz at a resonant frequency of 9 MHz.

Binding of enzymes to DNA and other molecular systems, in addition to other measurements involving luminescence, FTIR, and other phenomena, all provide information about the strength of the chemical bonds formed in chemical mixtures. The use of crown ethers to introduce specificity to certain molecular sizes is being pursued.

It is even possible to observe protein crystallization with such methods. Such a diagnostic could be quite valuable, as the conditions under which a protein will crystallize are very poorly defined. The importance of protein crystallization cannot be overstated, since it is with single crystals of proteins that the molecular structures of biologically important molecules may be understood, and from that, their behavior under chemical conditions.

Some considerations are being given to the concept of catalytic antibodies. This emerging field is based on the observation that if an antibody is designed in a shape close to that of an activated complex for a specific reaction, such a molecule is seen to speed up a chemical reaction by orders of magnitude. Thus the design of catalytic systems is becoming possible with the new tools as simple as the QCM.

## 2.6 Clusters and Quantum Dots

The terms "clusters" and "quantum dots" are used interchangeably in many cases. However, the term quantum dot appears to have associated with it phenomena that make a material property somewhat different than that of the bulk property of the same material. The term cluster seems to apply to any agglomeration of atoms that is not considered to be a single molecule. Clearly there is a wide overlap of the meaning of both terms. The optical properties of these materials are of considerable interest, as spectral shifts reveal confinement effects

due to the wall boundary conditions; recently luminescence has been observed that exhibits surprisingly narrow spectral features.

### 2.6.1 *Monodisperse Clusters*

Cluster physics at Cavendish Laboratory includes the production of monodisperse cluster samples that are size selected using magnetic selection techniques on charged cluster species (mass spectrometric separation). With the instruments available (or soon available) it is expected that the filtering of cluster sizes will be sufficiently precise as to remove clusters having one extra or deficient atom in 500. Interesting phenomena such as the magnetic behavior of rhodium clusters (which apparently is magnetic in the cluster and not in bulk) will be examined. The effects of coatings on clusters add additional variations of interest.

### 2.6.2 *Cluster Formation by Spin-Coating*

A direct and effective method of preparing a wide range of metallic and crystalline clusters with a fairly monodisperse range of particle sizes was described at Shell Laboratories, Amsterdam. Using spin-coating methods containing precursor salts, it was found that very small crystallite sizes could be produced on the surface of a silicon wafer [36, 37]. Compounds of copper nitrate, for example, could be readily produced by this method with particle sizes ranging from 4  $\mu\text{m}$  down to 4 nm. This treatment effectively gives the sample a "shock" treatment. The spinning sample produces a very thin film of solution (approximately one micron in thickness), and the rapid air flow over the sample evaporates the solvent quickly (about a second). This rapid evaporation of the thin layer of fluid produces an excellent distribution of crystallites with particle sizes ranging from 20 to 30 percent of the average size. Further chemical treatments (such as heating and hydrogenation) are used to produce catalytically active materials (such as copper clusters, in this case).

It has also been shown that when spin-coating is used with polymer precursors, the resulting polymer has a configuration that is "rippled" with the long axis in the direction of the centrifugal force, representing alignment of the polymer molecules from the forces involved.

### 2.6.3 *Clusters by Electrospray Techniques*

A method of fabricating clusters using an electrostatic spray technique is under investigation at Oxford University. In this technique a liquid solution is forced through a thin capillary that terminates at an electrode with several thousand volts applied relative to ground. The high field at the tip of the capillary causes the emitting liquid to form a "Rayleigh cone," which emits small droplets at a regular rate. Introduced into a dry atmosphere the droplets flash evaporate, leaving the solid residue to fall onto a surface. Surprisingly uniform sizes in the distribution are obtained by this method; under the proper conditions a spread in sizes of 0.1 percent is obtained, which is a fairly monodisperse sample. Rates of production of materials by this technique correspond to microliters of fluid per second. Samples that have been prepared by this method include GaAs [38], CdS [39], PbS [40], nitrides, arsenides, and metals. Some of these materials are deposited in conjunction with polymer precursors to form a dispersion and to avoid sintering of the aggregated clusters.

A most surprising observation has been made when silver nitrate (concentration about 0.001M in methanol) is extruded using this process. The high electric field (and associated charge balance) strips the anions from the sample, leaving silver metal in the droplet. When the solvent in this droplet evaporates, silver metal clusters result. Thus by starting with a silver nitrate solution, silver clusters (5 to 10 nm diameter) are produced directly. The plasmon resonance is observed at 500 nm for this material, with a width of about 200 nm.

## 2.7 Other

### 2.7.1 Local Probes As Machining Tools

Researchers at the University of Basel, Switzerland, have demonstrated the fabrication of small structures using mechanical forces resulting from an atomic force microscope (AFM) probe manipulating a polycarbonate surface in air [41]. Forces on the order of  $10^{-7}$  to  $10^{-8}$  N were used to "plough" 70 nm-wide  $\times$  10 nm-deep furrows into such a surface. By oscillating a silicon nitride tip at 4 KHz and over distances of 160 nm both laterally and vertically, characters could be written at a rate of approximately 200 nm/s with static forces of  $2 \times 10^{-8}$  N. Features (furrows) appear to be somewhat less than 100 nm using these techniques. This approach introduces the ability to mechanically shape nanometer-sized objects; the effect is probably due to the usual "plastic flow" recognized for deformation in such polymers. It is clearly too slow for information storage, but offers flexibility in exploring nanometer-sized circuits or other objects for mechanical properties. Microscopic features involving frictional effects and wear could possibly be better understood with such techniques; effects due to topographic structures, inhomogeneities, and grain boundaries may be investigated.

### 2.7.2 Fabrication of Nanostructures with Naturally Occurring Phenomena

A number of fabrication processes produce structures having nanometer dimensions through phenomena yet to be understood. One such process was mentioned at the Telekom Forschungs- und Technologiezentrum (FTZ) in Darmstadt, Germany. By passing argon or oxygen ions at  $45^\circ$  incidence over InP, the amorphosized InP took the form of ripples, very much like the ripples on the surface of a sandy beach after wave motion. The 80 to 1000 nm features are fairly regular, and represent another method of nanostructure fabrication [42, 43].

Alternative processes passing 4 keV argon ions over InP amorphosize the InP into clusters. These clusters appear as crystallites on the surface, and are fairly monodisperse, with dimensions of 50 to 100 nm. These crystallites have the same orientation as the substrate.

### 2.7.3 Silicon-Germanium

SiGe heterojunction material has been gaining increased attention at Delft. One objective is to observe behavior in vertical transport devices such as resonant tunneling diodes (RTDs). Some oscillations have been observed in areas of 10 to 100  $\mu\text{m}$  on an edge at low temperatures, but the oscillations disappear at temperatures above 80 K. A problem in working with this material is that the lattice match is not perfect, and hence significant strain is introduced with larger heterojunction interface area. This results in dislocations and non-ideal behavior as compared with the GaAs/AlGaAs used so frequently for such fabrication and measurements. Further, the mobility of electrons is only about 40,000  $\text{cm}^2/\text{V}\cdot\text{s}$  in SiGe at  $T = 4$  K, as compared with several million in GaAs heterojunction materials. One approach is to go to smaller areas where the lattice mismatch is less important. This has been done, but the voltage at which some effects are observed is shifted relative to the larger structures. Understanding the reason for these shifts is a current challenge; luminescence experiments on an array of quantum dots are anticipated in an effort to understand these phenomena.

### 2.7.4 Point Contact Fabrication in SiGe

In Delft, "point contacts" are being fabricated in a most straightforward and robust manner. A 40 nm-thick layer of silica is pierced with an electron beam to form a 10 nm diameter hole. Material is deposited on either side of the silica, filling the hole, forming a "point contact" 10 nm in diameter. SiGe behavior with small area conduction shows telegraph noise, characteristic of defect structures. This method of making "point contacts" will be applied to SiGe materials in an attempt to isolate a single defect, providing an opportunity to measure the properties of a single defect responsible for the observed behavior.



### 3. CHARACTERIZATION

Measurement of the properties of nanostructures is obviously critical to advancing the field. The discovery and use of local probes (such as STM, AFM, and near-field optical microscopy (NFOM)) is a major advance introducing new capabilities for this function. The use of transport properties has been a standard tool for decades; interference effects add an important level of complexity and flexibility to these properties. Spectroscopic tools continue to provide a great deal of insight to the unusual properties derived from confinement effects. Magnetic, mechanical, and even thermodynamic properties of nanostructures indicate remarkably new and/or versatile methods of characterizing the properties of these materials.

#### 3.1 Local Probes as Characterization Tools

A variety of local probes have been introduced since the discovery of the STM. A brief review of the use of STM for the characterization of materials has recently appeared [44]. Phenomena associated with bulk properties that have either short wavelengths or a localized interaction distance seem to be appropriate for use as local probes. Nonlinearities in the STM signal have been observed [45] and shown to provide information about doping profiles in semiconductors [46]. The use of STM for analysis of cross-sectional features of heterojunction semiconductors is revealing information about depth profiles [47, 48]. The number of material properties becoming accessible for measurement at nanometer dimensions is truly opening vistas of major proportions.

##### 3.1.1 *Surface Reconstruction Observed with Scanning Force Microscopy*

There are many examples in the literature of using local probes for examining surface reconstruction patterns. Both STM and AFM have revealed hundreds of patterns documented in the literature. Using scanning force microscopy (SFM) for such information is more difficult under ultra-high vacuum conditions for reactive surfaces due to destructive interactions between the tip and the sample. By mechanically introducing teflon (polytetrafluoroethylene, PTFE) on the tip prior to surface examination, surprisingly clear SFM images of Si(111)  $7 \times 7$  have been obtained [49]. Lateral force data exhibit the symmetry of the reconstructions with such tip treatments. One conclusion reached is that PTFE appears to be a good "lubricant," even on the atomic scale.

SFM has also been used to examine surfaces of salts such as sodium fluoride in Basel, Switzerland. Atomically resolved features demonstrate stronger interactions between the tip and the ions for one charge relative to the other in ionic salts. The force variations in the vertical (normal) direction are two orders of magnitude smaller than those in the lateral direction. The difference in the magnitude of these forces is a subject of continuing investigations.

##### 3.1.2 *Scanning Ion Conduction Microscopy*

This form of microscopy involves yet another variation on the array of scanning probe microscopies appearing in the research community. This technique involves the use of a narrow ( $0.1 \mu\text{m}$ ) orifice filled with and immersed in an electrolyte. An electrical lead in the capillary and one in the electrolyte solution forms a closed circuit through which current may be measured. As the fiber tip is brought close to a surface, the area around the tip of the fiber is pinched off, changing the resistance of the circuit. This represents the basis for an image as the fiber is scanned across a sample. Samples may be scanned with about  $700 \text{ \AA}$  resolution by this method. The study of corrosion processes appears to represent one area in which this probe may be exploited. Surface topography, ion conduction behavior in a solid, and various other phenomena will be examined with this instrument at the Westfälische Wilhelms Universität, Münster, Germany.

### 3.1.3 *Optical Microscopy with Local Probes*

A general introduction to the spectroscopic methods used with local probes (STM cathodoluminescence and NFOM) has recently appeared [50]. Optical and spectroscopic information is becoming available at dimensions far smaller than the traditional diffraction limited spot size with these tools.

A method of fabricating a tip for NFOM is being pursued in Münster based on the manner in which a piece of glass breaks to form a carefully defined apex in a wedge. Subsequent vapor coating of this break with slant-deposition of aluminum provides a bright emission point for these experiments. Lateral resolution of better than 30 nm has been achieved with these tips.

Scanning tunneling luminescence (STL) involves observing the luminescence spectrum of a sample excited by electrons from a tunneling tip. Information about surface geometry, defects, edge discontinuities, band-bending, and depletion widths at an interface may be obtained with these probes [51-53]. At IBM, Zürich the spectral features are seen to be functions of the sample thickness as well as the doping conditions in a GaAs sample [54] and an AlAs/GaAs superlattice [55]. Atomic resolution of the luminescence process as a function of sample position has also been reported [56].

Emission of photons from STM-stimulated plasmon excitation has been studied as a function of materials, dielectric properties, and tip distance at IBM, Zürich [57].

### 3.1.4 *Shear-Force Optical Microscopy*

Another form of microscopic probe under investigation in Münster involves shear-force optical microscopy, in which the vibration of an optical fiber tip is sensed with a helium-neon laser. As the tip approaches a surface, the vibration is damped due to the viscous fluid between the two surfaces. The reduction in the vibration amplitude may be sensed as a function of scan position in a raster, revealing additional details about the mechanical nature of the surface.

### 3.1.5 *Near-Field Acoustic Microscopy*

This form of microscopy involves the oscillations from a quartz crystal tuning fork. The tuning fork in use in Münster, Germany oscillates at 32 kHz; one corner of the fork is scanned across a sample (in air, in this case). The frictional force due to a fluid in the intervening medium damps the vibrations of the tuning fork. Closer spacing increases the amount of damping, which represents a change in the signal and the basis for a raster of information. The resolution of this instrument is now approximately 0.2  $\mu\text{m}$ .

### 3.1.6 *Biological Materials Characterized by Local Probes*

AFM and STM of biological molecules has presented some difficulties due to the forces and subsequent motion between probe and molecule. This has resulted in poor images or irreproducible results in many cases. The method of dynamic force microscopy (DFM) is introduced at Basel, Switzerland in which the probe vibrates close to its natural resonant frequency at amplitudes of 5 to 30 Å. The resonant frequency shifts when the force gradient changes, changing the amplitude (of an off-resonant frequency). This provides a signal for an improved image of molecules with good resolution [58]. One to three angstrom corrugations in DNA strands may be observed, for example. Some broadening of the strand width was observed relative to expected values, most likely due to the finite dimensions of the probe. Images of Tobacco Mosaic Virus were also obtained. The vertical resolution is estimated to be less than one angstrom, and the lateral resolution is 1 to 3 nm (depending on sample). It was found that deposition



of the molecules onto an LB film was helpful in observing these soft biological materials. Local probe imaging of materials such as globular protein vicilin have been examined [59].

### 3.1.7 Magnetic Force Microscopy on Superconductor Materials

Magnetic force microscopy (MFM) at Basel, Switzerland has successfully imaged single vortices frozen in a yttrium barium copper oxide (YBCO) thin film at 77 K. This appears to be the first demonstration of MFM imaging of a single vortex in high temperature superconductors at these temperatures [60-67]. High temperature superconducting materials have short coherence lengths and high vortex mobilities as well as complex crystalline structures. For this reason, it is very difficult to observe vortices in these materials, although in other lower temperature superconducting materials such vortices have been observed. Lateral forces on the low  $10^{-13}$  N range were measured with the magnetically sensitive tips used in these experiments. The ability to correlate topographical features with magnetic images may give new insight as to the nature of the pinned vortices in such materials.

### 3.1.8 Probe of Dielectric Breakdown

One program at Cambridge includes "Fowler Nordheim imaging," in which the characteristics of a semiconductor interface beneath a silicon oxide surface may be observed. The mean free path of the electrons from a conical diamond tunneling tip are sufficiently long that the image may be obtained through oxides 100 nm thick. Lateral resolution approaches the separation of the tip from the interface being examined. A critical question here involves the breakdown mechanisms in oxides [68]. Asperities at the edge of an interface are critically important for nucleating this breakdown. Statistical effects become very important as they are much larger for thin film interfaces.

### 3.1.9 Lubrication Properties

The atomic force microscope (AFM) is being used to examine lubrication effects at the solid-liquid interface [69] at Cambridge. The forces as a function of distance reveal formation of the molecular layers; this form of microscopy is termed atomic force spectroscopy (AFS), since the signal varies with distance. With this, the stiffness of consecutive intermolecular layers may be examined [70]. Considerable effort is being devoted to force interactions in liquids, including friction imaging and coefficients of friction.

### 3.1.10 Thermodynamic Sensors

Calorimetric information for very small sample sizes may be observed experimentally by using a bimetallic layer and light deflection is proving to be a very sensitive measure of the thermal changes from chemical reactions [71]. Sensitivities of approximately 1 pJ have been reported with a silicon probe having dimensions  $35 \times 400 \times 1.5$   $\mu\text{m}$ . A 0.4  $\mu\text{m}$  coating of aluminum forms the bimetallic layer.

By using bimetallic strips having dimensions of 2  $\mu\text{m} \times 20$   $\mu\text{m}$ , it is possible to look at less than one femtojoule of energy absorbed by measuring the optical deflection off the metal strip [72]. The light is modulated at 1000 Hz; detection is with phase sensitive methods. By shining light on a metallic surface containing a molecular monolayer, the spectrum of the adsorbed species may be observed! The power on the strip is about 2 to 20 nW; the strip used experimentally thus far has a thermal relaxation time of about 0.5 ms. It is anticipated that the metabolism of a single cell may be measured with this apparatus.

Photosynthesis processes include critical steps where light is "harvested" by absorbing molecules, and the energy is subsequently passed along molecular chains where it is deposited in chemical reactions leading to the storage of energy through the production of sugars. Researchers at Cambridge are working

with the University of Sheffield where this process has been under study for some 15 years. The current experiments are intended to use the cloned reaction centers responsible for passing the energy along a chain of molecules. Once these samples are available, picosecond pulses induced by lasers are to be measured. The propagation behavior of these excited states is not well understood; information about this behavior may be forthcoming with these experiments.

### 3.1.11 *Scanning Frustrated Total Internal Reflection Microscopy*

A relatively new form of scanning probe microscopy was mentioned in Enschede, The Netherlands. The Scanning Frustrated Total Internal Reflection Microscopy (SFTIRM) is based on the breakdown of total internal reflection at a surface. Total internal reflection is obtained whenever the angle between the propagation vector for light and a surface is below a critical angle. If a scanning probe is placed in the region of lower index of refraction (the region in which light does not pass), the perturbation on the evanescent wave from the light being reflected will pass light through to the other medium. The degree of transmission is sensitive to the distance between the scanning probe and the surface. Variations in topography or surface conductivity/potential represent the means of obtaining an image from a raster scan. A resolution of 50 nm has been obtained with this device.

### 3.1.12 *Surface Acoustic Waves and Local Probes*

The tunneling current through an STM probe is a nonlinear function of the applied voltage. This nonlinearity turns out to be the key ingredient for sensing acoustic waves with an STM tip. The tip is placed in close proximity to the surface of a surface acoustic wave (SAW) device operating at 35 MHz. An oscillating voltage is applied to the tunneling tip at 35.01 MHz. The distance between the tip and sample is about 5 Å; the SAW oscillations vary that distance by about 1 Å. An amplification stage tuned to the difference frequency of 10 KHz senses the amplitude and phase angle associated with this oscillating distance [73, 74]. Images using this device have not yet revealed atomic resolution, but good resolution of grain structures in gold samples is obtained. Interesting information is available by comparing the amplitude and phase information with images obtained from an STM (each gives different images, although the gross features have a resemblance) [75, 76]. The in-phase amplitude is associated with the vertical motion of each portion of the gold surface, whereas the out-of-phase amplitude is associated with the horizontal motion of the particles that are moving in an elliptical orbit [77]. The amplitude and phase information thus provides a measure of the inclination angle at that portion of the sample. Variations are being examined at the Paul Drude Institute, Berlin to exploit the unusual aspects of this instrumentation.

### 3.1.13 *Modeling of Images Using Local Probes*

Modeling of images obtained by STM and AFM is a non-trivial exercise, but it is very important for understanding the image details produced with these tools. The density of states and the perturbation of energy levels for molecules and atoms in the presence of an electric field (e.g., produced by an STM tip) have been modelled [78]. Forces involved in distorting a molecule with an AFM tip have likewise been modelled extensively and compared with experiment in Toulouse, France. Systems that have been calculated include carbon (in graphite), gold on the Au(100) surface, benzene on Ru(111), phthalocyanine on Cu(100), Xe on Cu(110) at a step, and buckminsterfullerene on Au(110) [79]. The resulting software is becoming available at other laboratories and should be a useful adjunct for interpreting images obtained by local probes. Recent results have modelled the AFM and STM images of buckminsterfullerene on a gold surface.

Additional modeling efforts are directed at the dynamic behavior of gold atoms when in contact with an STM tip. These efforts are aimed at predicting the motion of gold atoms on a NaCl surface [80], and the

formation of single atoms as well as clusters of gold atoms (two to three atoms) using STM tips for manipulation.

### 3.1.14 Miniature Electrodes and Electrochemistry

Microelectrodes have been introduced into electrochemical observations for a number of years. By making the electrode area sufficiently small, and by flowing the solution over the electrode at rapid speeds, the electrochemical probe becomes a method of observing the kinetics for fast reactions. Research at Oxford has been examining this technique using 4  $\mu\text{m}$  "bands" of metal over which solutions flow at rates of 100 miles/hour in the center of a 50 to 100  $\mu\text{m}$  gap. Voltage fluctuations of up to  $10^6$  V/s may be observed by this technique over a 1  $\mu\text{s}$  time frame. With this probe, the usual voltammetric curves obtained with triangular voltage sweeps become smooth "S-shaped" curves [81] with minimal effects due to the electrical double layer, and capacitance charging. With this instrumental approach, it should be possible to obtain diffusion rates of ions as small as the hydrogen ion, which limits the rate of many acid-base reactions.

### 3.1.15 Molecular Electronics

In Europe the term "Molecular Electronics" at first started out with somewhat of an uncertain direction. As research evolved, it eventually became interpreted as the activities associated with the electronic properties of molecular systems. The two directions in which molecular electronics seems to have the most direct payoff technologically are 1) the study of molecular materials of direct interest for electronic device fabrication, such as the use of resists, and 2) the use of electronic properties of molecular materials for sensor applications, as is being done at Tübingen, Germany. Some steps are being taken at Tübingen to carefully fabricate and characterize molecular structures and to measure transport properties.

The subject of molecular electronics has been addressed in a recent paper [82] from Stuttgart. As transistors or active elements of an electronic circuit as we know them today, such molecular materials are likely to be slow and unacceptable for most purposes involving logical operations in computation. Solitons in molecular systems often tend to be pinned, hence not mobile nor operating in a manner which may be useful (at the present time).

## 3.2 Transport Properties

Transport properties represent the basis for electronics, and as such is exceptionally important to understand in detail. Transport properties in thin films and in nanostructures represent a wealth of new behavior relative to that observed in bulk materials. High mobility behavior in heterojunction materials has introduced a wealth of phenomena associated with interference, confinement effects, and depletion behavior. Magnetotransport phenomena is another area revealing many additional details about charge transport.

One of the most unusual and interesting developments pertaining to charge carriers within the past decade is that of the quantized conductance of small point contacts. The split gate originated with work of Trevor Thornton and David Whareem at Cavendish Laboratory. It has been used at Delft and Eindhoven to discover and characterize the surprising behavior of point contacts and quantized conductance observed at low temperatures. As such, this represents a significant step forward in understanding transport behavior, although this behavior is not critical for understanding many other aspects of charge carrier behavior.

The quantum Hall effect was discovered by von Klitzing at the Max Planck Institute in Stuttgart. Subsequent behavior involving magnetotransport has revealed additional physical phenomena.

Magnetotransport is becoming a useful tool to probe the properties of nanostructures. Many additional aspects of these phenomena are currently under study.

Transport properties of conjugated polymers are being examined in Mainz, Germany to understand the band gap properties of these molecules. A low band gap is hoped for in these materials such that they will demonstrate high conductivity with low doping levels. Phenomena such as Pierels distortion lead to limitations of the band gap that can be produced with molecular systems. These effects are not yet understood, and provide a rich source of phenomena for scientific inquiry.

### 3.2.1 *Quantized Conductance/Point Contacts*

Quantized conductance continues to attract interest [83, 84]. At temperatures of 20 mK some oscillations have been observed in Delft at the upper end of the usual steps for the I-V curve. These oscillations are attributed to interference effects between reflected electrons at the anode region of the conduction device interfering with electrons traversing the squeezed conduction region of the orifice traversing the quantized states for conduction.

The effects introduced by application of a magnetic field show the evolution of conductance steps at  $2e^2/h$  in the semiconductor to  $e^2/h$  in high magnetic fields. The magnetic fields break the spin degeneracy, hence there is only one kind of conductor (spin up or spin down) for each conduction channel at higher fields. This work was also completed at Delft.

A number of the researchers associated with the original observation of quantized conductance were at Philips Laboratory, Eindhoven. Some of the experiments performed at Eindhoven appear in an earlier paper [85]. One of these researchers, now at Glasgow, described an interesting observation. The usual channel formation through the split gate and depletion effects was examined with unequal voltages on each of the split gate electrodes. These voltages were applied to maintain an overall constant voltage of the two combined gate electrodes. With such an arrangement, the potential well through which electrons travelled could be "tilted" and moved in either transverse direction. The results of this original experiment were published recently, but not published was the direct observation of the transverse structure of the wave functions traversing the conduction channel. By properly displaying the conduction/voltage curves, it is now clear that the square of the transverse portion of the electron wave function may be directly obtained experimentally. They match the densities predicted by the usual solutions of an harmonic oscillator in elementary quantum mechanics. This is a beautiful text book display of the solution of these quantum mechanical problems.

### 3.2.2 *Single Electron Devices*

A discussion of single charge tunneling events presents a useful reference for a general view of these phenomena associated with superconductors [86]. The basic phenomenon associated with the coulomb blockade (a manifestation of single electron devices) has been studied extensively by a number of groups for more than five years [87]. Philips Laboratory, Eindhoven, has worked with single electron effects in the past [88-90], and was one of the first to observe these effects at room temperature [91, 92]. The first unambiguous observation of the effect was at AT&T Bell Laboratories in 1987.

A group at CEA, Gif Sur Yvette, France has modelled the possible utilization for memory and logic devices as well as for current standards and electrometer devices. The phenomenon envisioned for memory or logic requires a high degree of reliability, which has been examined in recent papers from CEA. The potential utility is envisioned for their use as electrometers and as current standards. The introduction of single electron devices using superconducting materials involves the Cooper pair as a charge carrier. The

physical manifestations of the Cooper pair is observed experimentally at CEA, and the advantages of using superconducting materials with these structures is under active investigation.

There seems to be a complete analogy between single electron devices and electronics of today [93]. These devices will make ultrasensitive electrometers and probably useful current standards. The one possible problem foreseen is that the input/output isolation appears to be difficult. Devices will need error correction to compensate for bit errors due to probable uncontrolled transitions.

Further limits associated with this device as a practical transistor are associated with the voltage driving the number of electrons on the island. It is extremely difficult to eliminate effects due to stray charge in such a device. This stray charge causes fractional changes in the voltage (hence the charge on the island) controlling the passage of current, and results in a drift instability that is difficult to control. One could adjust each device for the characteristics observed, but this would be a monumental task. This limitation, along with other difficulties, suggest that this device is unlikely to be useful in digital logic devices.

The "electron turnstile" is a device that passes electrons one at a time in synchronism with an applied voltage (or electric field). Such a device was developed at CEA and Delft. Frequency limits of the electron turnstile are of interest as they relate to the absolute accuracy with which currents may be measured. This limit is 20 MHz, due largely to the limiting resistance of  $h/e^2$  which is 26 K-ohms. The accuracy possible with this device is the subject of a recent publication [94].

In the spring of 1994, an electrometer device was fabricated at Delft with a sensitivity of  $8 \times 10^{-5}$  electrons/ $\sqrt{\text{Hz}}$ . This device consisted of two junctions across a quantum dot controlled with a gate voltage. The capacitance at each junction was  $10^{-16}$  farads, corresponding to a thermal energy of 2 to 3 Kelvin. This device is claimed to hold the world's record for sensitivity of electrometers at that time. The sensitivity of this for measuring charge may be compared with the sensitivity of SQUIDS for measurement of magnetic fields. This instrument is now considered to be a tool to investigate other phenomena involving charges with very sensitive measurements never before possible.

Some experiments are under way at Delft in which the coulomb blockade phenomenon in the presence of a magnetic field is observed. The specific example at 10 mK is one in which the first (and largest) orbital motion of an electron just "fits" within the space available (600 nm diameter containing 300 electrons for this example) for a quantum dot between two conduction channels (or barriers) [95]. A second occupied Landau level under these conditions (or quantum Hall state) occupies a smaller spatial region (at higher magnetic fields). Most of the tunneling of conduction electrons into the quantum dot region is from levels having equal orbital quantum numbers (to first order). This, of course, gives rise to a large number of sharply defined peaks as a function of voltage, each peak corresponding to a change of one electron in the dot. As the magnetic field increases some of these peaks split, combine, and split again. The magnitude of the splittings is equal to the energy of the quantized flux unit.

When two peaks in an applied magnetic field overlap, near degeneracy of two states occurs. The degeneracy corresponds to different numbers of electrons on the dot. If measurements are made over a prolonged period while sitting near one of these pairs of peaks, it is seen that a switching occurs between two Landau levels by a single electron. This switching time is observed at Delft to occur at rates on the order of 10 to 200 s in magnetic fields of some 4 to 6 Tesla. The spatial ring between first and second Landau levels operates as an incompressible quantum Hall fluid acting as a tunnel barrier. This work has been submitted to *Physics Review Letters*.

Future experiments at Glasgow associated with quantum dot behavior will try to demonstrate the effects at higher temperatures. This, of course, requires smaller feature sizes. Various depletion phenomena will be used in attempting this. It is postulated that 10 nm dots with 2 nm spacings will demonstrate these effects at room temperature.

Additional work has been done at Bagneux with the coulomb blockade phenomenon involving small 2-D electron islands with GaAs/AlGaAs heterojunction materials [96]. The interesting question regarding the use of a single molecule as the island for a single electron device was posed. The major problem there is controlling the gate voltage (on a single molecule!). This could be a very challenging research problem for the future.

Single electron devices involving superconducting material demonstrate somewhat different behavior. A typical structure for a coulomb blockade device in which the island is made of superconducting material demonstrates the consequences of the Coopers pair. A magnetic field applied to such a device changes the nature of the steps observed in the current-voltage curve. In zero magnetic field the steps occur in accord with the charge of two-electron carriers. As the magnetic field is applied, the free energy difference of placing a single electron in a higher energy state (the superconducting gap) is observed. Thus the single step involving the two-electron Coopers pair is split into two closely spaced one-electron steps. This is true as long as the superconducting gap is less than the coulomb energy charging the capacitor. At yet higher magnetic fields, where the superconductor goes normal, the usual one-electron steps are observed [97].

More recently a superconducting single electron transistor (superconductor-gap-superconductor-gap-superconductor with a gate on the center superconductor) has been fabricated and characterized. The current-charge relationship shows the usual oscillation at zero magnetic field. However when the magnetic field is introduced, the peaks at odd intervals of the charge/electron charge show dips on each peak due to the introduction of a quasiparticle in the island [98].

Further investigation into the coulomb blockade behavior of superconducting materials is anticipated at CEA. Because the carrier has a charge of two electrons in superconductors, the charging energy  $q^2/2C$  of a capacitor is greater, hence the effect may be observed at higher temperatures, and the periodicity of the oscillations in the current-charge relationship is  $e/C$  rather than  $e/2C$ . The advantages introduced by this factor of two are being explored in a systematic manner.

In the area of single electron effects researchers at Chalmers University, Göteborg, Sweden have worked with stacking a number of stages (15 to 20) of the traditional barrier-well-barrier configuration [99, 100]. This stacking provides a superior reliability in the passage of single electrons. Imposition of an external frequency to the single electron device has produced a "blip" in the current-voltage relationship where the electron passing frequency equals the external frequency, indicating phase locking. Variations involving the single electron turnstile and pump configurations that involve sequences of these barrier configurations are under way here. Coulomb blockade effects have been noted here for Cooper pair tunneling [101-103] in superconducting materials. It is noted that by using a superconducting flux transformer, the feeble current passed through a single electron device (pump or turnstile) can be multiplied by factors of  $10^3$  to  $10^4$ , enhancing the capability of fabricating current standards for larger values of current. An alternative to using the superconducting flux transformer is to couple two multi-junction devices capacitively, where several in series are coupled to several in parallel. With this arrangement, a similar multiplication of current may be obtained.

An interesting note involves the basic constants associated with single electron devices (which potentially can measure the electron charge  $e$  accurately), the quantum Hall effect (which measures  $h/e^2$  accurately), and the Josephson Junction (JJ, which measures  $h/2e$  accurately). These basic measurements,



along with the fine structure constant, all give independent measurements of the fundamental constants. At some point in the future, the accuracy of these independent measurements could become inconsistent, requiring a redefinition of some of these basic parameters in terms of the others.

### 3.2.3 Apparent Single Electron Devices at Darmstadt: Field Emitter Devices and Coulomb Blockade Phenomena

New designs for field emitters to protect against electrostatic discharges and transients are of interest to companies such as Daimler-Benz. This is being investigated with a variety of n-doped GaAs field discharge devices at the Technische Hochschule Darmstadt. Device design here consists of GaAs single crystal "triangles" positioned 0.3 to 0.5  $\mu\text{m}$  from an anode [104] (see Fig. 6). An attractive feature of such a geometry is that the distance between anode and cathode is on the order of the mean free path of molecules in air. Thus electric discharges are not supported, and the performance is that expected of a device in a vacuum, without the requirement for a vacuum. With a bridge 30  $\mu\text{m}$  long and a radius of curvature of 25 nm across 0.3  $\mu\text{m}$ , a current of 60 mA can be switched. Placement of these in parallel can give substantial protection for the purpose of discharging undesired voltage surges.

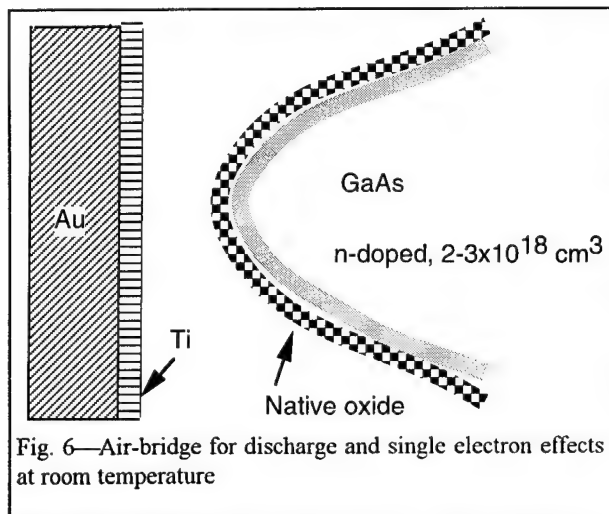


Fig. 6—Air-bridge for discharge and single electron effects at room temperature

These discharge devices may be designed with triode performance by introducing a gate as another "triangle" either side of the cathode. These devices show excellent I-V characteristics with a turn-on anode voltage of about 7 V. Doped semiconductors used as cathode materials have the advantage of limiting the occurrence of "hot spots" on the cathode wedge. If a higher emission rate occurs along one position of the cathode, the surface screening charge is reduced and the field at the emitting edge area of the wedge penetrates into the semiconductor, limiting the discharge in this region. Thus the design is self-limiting and results in a smoothly operating device. Additionally, by broadening the wedge at the ends to electrically conducting pads, the hot spots that would

form at the ends are eliminated. The Technische Hochschule Darmstadt has a patent pending for this design. The triode is a set of interdigitated fingers, with one alternate pair serving as the gate, the other serving as the anode.

The I-V characteristics of these devices show steps caused by the "low capacitance" design. These steps are believed to be due to coulomb blockade phenomena at room temperature [105-107]. The overall capacitance of the device (30  $\mu\text{m}$  length with a 25  $\mu\text{m}$  radius of curvature on the knife edge, with a spacing of 0.4  $\mu\text{m}$ ) is  $10^{-17}$  to  $10^{-18}$  farads. With a current of  $10^{-8}$  A at a voltage of 0.1 to 0.2 V, a number of distinct ramps in the current/voltage relationship is observed. Just how this can occur is a bit of a question, but it is believed that there is a thin oxide layer on the surface of the semiconductor. The potential function appears to be one of two steps (spatially), one for the oxide, and one for the vacuum. This may be represented as two barriers at different heights. In an electric field, a slope is given to these two barriers as the overall potential is modified from high to low voltages. A dip at the bottom of the lower potential well acts as a sink for electrons transitioning the barrier profile. Perhaps this accounts for the coulomb blockade behavior.

Still more puzzling is the behavior observed when the differential resistance,  $dR/dI$ , is plotted against voltage. It is seen that the  $dR/dI$  takes on specific values rather than that of a continuum, as would be

expected if the steps occurred with a smooth S-shaped curve from one step to the next [108]. Such behavior is not readily understood and may be related to chaotic behavior of such a system.

### 3.2.4 *Interacting Charge Carriers*

One of the principal problems associated with the use of heterojunction materials and depletion effects due to side (or split) gating is that the spatial resolution of these devices is limited by the vertical spacing between the side gate and the 2-DEG. This distance has not been reliably prepared with much less than 300 Å (due to surface effects and statistical fluctuations in dopants that significantly reduce the carrier mobility in the 2-D carrier gas). Consequently, lateral feature dimensions much smaller than 300 Å are not readily available.

Alternative ways of obtaining smaller features with independent control of each channel are being sought at the Cavendish Laboratory in Cambridge. GaAs/AlGaAs heterojunction materials are primarily used; some work is also done with InSb. One such way is to prepare the 2-D carrier channels imbedded within the semiconductor material. If both channels are imbedded and away from near surface effects, then closer distances may be prepared for observation. The problem remains, however, in making electrical connections with each channel independently without exposing either to a surface. For this challenge, focused ion beam (FIB) deposition is introduced during growth of the heterojunction material. This is termed Focused Ion Beam Molecular Beam Epitaxy (FIMBE). An older system has demonstrated the viability of such ideas with 10 μm resolution. A newer system is being built that will provide 0.1 μm lateral resolution to the features imbedded in the heterojunction material during growth. Ion implantation of gallium can make an effective insulator of selected regions of the implanted material.

Once two parallel 2-DEGs have been fabricated, the challenge of making a connection to each with two different electrodes is accomplished by adding one gate on the "top" of one side of the structure and a second gate on the "bottom" (back gating) [109, 110]. By applying appropriate voltages to the top and bottom gate, depletion effects break the connection to one or the other conduction channel. With conducting leads at either end of these conduction channels (tin, silicon, or beryllium introduced by the FIB during heterojunction growth) one now has two 2-D gases in close proximity. Voltages to each channel may be controlled independently. The distance between the layers with these fabrication techniques is expected to be 7 to 20 nm. With such devices the laboratory expects to be able to look at resonant tunneling diode effects, electron drag, electron-electron interactions between 2-D gases, and even electron-hole interactions.

### 3.2.5 *Magnetotransport Phenomena*

Researchers at the Max Planck Institute für Festkörperforschung, Stuttgart, are continuing research in the area of magnetotransport phenomena associated with potential functions that have been introduced by regularly spaced lateral perturbations in a 2-DEG [111-114]. The measurements are taken in a manner very much like the measurements of the quantum Hall effect. The heterojunction material is prepared by normal epitaxial growth methods, and then patterned with arrays of holes etched into the heterojunction material, thus perturbing the structure of the 2-DEG with a modulated potential function in a regular square lattice array. The degree of etch (and, hence, the magnitude of the perturbation) as well as the lattice spacing and hole size all represent variables that have been investigated. One example of the many etched patterns under examination was a lattice of 10 nm holes etched in a 60 nm lattice spacing.

As the Hall resistance is measured in these materials, the behavior at low magnetic fields reveals regular fluctuations representing commensurability oscillations, as the orbital diameter of the electrons match the spacings in the arrays. These appear as oscillations at low magnetic fields in addition to the



usual quantum Hall oscillations. The predictions of the locations of these oscillations match experimental observations quite well. The width of the oscillations is due to the chaotic motion of the electron orbits in the structured lattice. The effect of chaotic motion in limiting these line widths has not yet been modelled successfully.

Related observations at Glasgow involve magnetoresistance measurements in lateral superlattices used as gates on transistors. The diameter of the electron carriers decreases with increasing magnetic field. As this diameter crosses sequential steps of the superlattice, commensurability oscillations are observed in the conductivity. Second harmonics were observed experimentally in such devices. Models have explained the presence of these oscillations in terms of a strain field in which the potential function is peaked rather than oscillating in a strictly sinusoidal manner.

### 3.2.6 Hole Mobilities

One of the accomplishments of which Nottingham is justly proud is the production of heterojunction materials that demonstrate high mobilities for hole carriers [115]. The "world's record" has recently been produced on the (311A) plane ("A" designates the gallium atoms) of GaAs/AlGaAs. The low temperature mobility of the holes in this structure is observed to be  $1.2 \times 10^6 \text{ cm}^2/\text{V-s}$  (as compared with a comparable value of  $10^5$  on the (100) plane). This was achieved with carrier concentrations as low as  $0.8 \times 10^{11} \text{ cm}^{-2}$ . Above 4 K the mobility is limited by phonon scattering, and below by interface scattering. This work should appear soon in *Applied Physics Letters*.

With these high mobilities and low carrier densities, it is possible to map out the structure (density of states) of the holes in the valence band [116]. This information has been exceedingly difficult to determine by other methods [117, 118].

The Nottingham group has been active in investigating a number of phenomena associated with molecular beam epitaxy growth on higher-order planes in GaAs/AlGaAs systems. Double resonant tunneling devices have been investigated on such planes.

### 3.2.7 Impurity Sites as a Probe of Density of Incoming Electrons

By selecting resonant tunneling diode (RTD) structures (double barrier) with a few impurity sites in the well region of the structure, it is possible to probe the energy density of the impurity sites [119]. This is possible because transmission through the first barrier region is maximized by satisfying resonance conditions, where the energy of the incoming electrons is equal to that of the impurity sites within the well. Structure on the current-voltage curve for samples prepared at Nottingham demonstrate considerable structure in addition to the usual peaks associated with the RTD.

### 3.2.8 Tristability in a Resonant Tunneling Structure

Bistability in the current-voltage relationship of a double barrier structure has attracted recent attention [120-122]. Electrical noise in such a circuit may cause switching between the two bistable states. A more recent observation at Nottingham has demonstrated tristability for these devices at temperatures below 150 K [123]. This was accomplished with a specially designed circuit using a positively sloping load line.

### 3.2.9 Chaotic Behavior in Interference Devices

The nature of high mobility materials is to allow interference effects in larger structures than is otherwise possible with materials having lower mobilities. With this feature, chaotic behavior may be

observed by measuring the conduction behavior in nanostructures having "arena-shaped" and trapezoidal-shaped boundary conditions. In magnetic fields tilted relative to the perpendicular to the plane of a 2-DEG at low temperatures, such a structure demonstrates chaotic current-voltage relationships [124, 125].

### 3.2.10 *Transport Properties of Gold Wires*

With the fabrication technique using four LB layers as a resist (described in Section 2.1.6.2), the magnetoresistance of 20 nm gold wires was measured at the Katholieke Universiteit Leuven. A change in the resistance of about 1 part in  $10^4$  was observed at fields of about 50 gauss due to a quenching of one relaxation mechanism due to interference between electron conduction paths that result in constructive/destructive interference after transiting along different paths (analogous to Aharonov-Bohm effect, but along uncontrolled irregular paths). From these measurements the mean free path for electrons in gold was measured to be 1.2  $\mu\text{m}$  at 1.2 K and 0.8  $\mu\text{m}$  at 4 K.

### 3.2.11 *Transport Properties of Carbon Tubules*

Using the fabrication capabilities of local probes, gold leads have been used to make contact with a 50 nm diameter bundle of carbon tubules prepared by hot plasma techniques. The two-probe resistance of carbon tubules has been measured as a function of temperature and magnetic field [126]. The resistance of these tubules varies by more than a factor of two between temperatures of 10 and 100 K, and shows a remarkably steep drop below 1 K. It also demonstrates a marked 30 percent decrease in resistance with magnetic fields of greater than 12 T at these temperatures, an effect that is yet to be fully explained. This variation in resistivity is presumably a change in the bulk resistivity and not dependent on the geometric or confinement effects of the nanostructure.

### 3.2.12 *Universal Conductance Fluctuations*

Universal conductance fluctuations may be observed on a large number of nanostructures due to interference effects as many different transport paths interfere with one another. These fluctuations are seen to be a sensitive function of magnetic field, displaying many extrema as the resistance fluctuates in a complex but reproducible manner. Researchers at the Katholieke Universiteit Leuven, Belgium, have observed irreversible behavior of these fluctuations after maintaining the sample at high magnetic fields for periods of time. This is due to a hysteresis phenomenon, where apparently a crystalline arrangement changes with time. The pattern is very sensitive to small changes in atomic displacement within a nanodimensional sample, and this sensitive measurement is being investigated as a diagnostic technique for determining small changes in atomic rearrangement in a solid state sample.

### 3.2.13 *Superconducting Materials and Nanodimensions*

Transport behavior in nanostructures made of superconducting materials offers substantial opportunities to investigate new phenomena [127]. The behavior of single-electron devices fabricated with superconducting materials is covered in Section 3.2.2. Additional effects are mentioned here.

Interference effects are, of course, due to Cooper pairs, which carry twice the charge as that of a single electron. Coherence lengths in normal (i.e., not high temperature) superconducting metals approach those of high mobility semiconducting materials (about 1  $\mu\text{m}$ ). A major difference exists with confinement effects. Whereas the wave function of normal electron carriers approaches 0 at an infinite potential barrier, the gradient of a wave function approaches 0 for a superconducting charge carrier. This results in remarkably different behavior.

Amplitude variations for the Aharonov-Bohm fluctuations in semiconductors are nominally one part in  $10^5$ ; in a comparable experiment involving superconducting materials, the effect (referred to as the Little-Parks effect) is nearly 100 percent. A ring conductor in a magnetic field behaves in a manner similar to that of a SQUID, oscillating between normal and superconducting with flux quantization in the ring. By fabricating nanostructures in a 2-D superconducting layer the flux lines can be pinned to specific sites [128]. Imposing patterns for these nanostructures can result in specific flux pinning behavior determined entirely by the nanostructures in the material.

### 3.2.13.1 Semiconducting-Superconducting Junctions

A program at Cavendish Laboratory involves the transit of charge carriers from semiconducting to superconducting regions of a semiconductor/superconductor junction. Transport across this interface involves Andreev reflection in which the one-electron carriers of the semiconductor transform into the two-electron carriers of the superconductor plus a hole travelling in the opposite direction. A peculiar symmetry is observed as the voltage of these junctions is swept across zero voltage. Although the material combinations would not suggest a symmetric I-V curve, observations appear to support that. Perhaps there is a universal superconductor-normal-superconductor (s-n-s) junction which is independent of the material across such boundaries. This work is pursuing answers to such intriguing questions.

Studies of Andreev reflection involve the conversion of an electron charge carrier to a Coopers pair have been reported [129, 130]. Conduction is observed from a superconductor to a semiconducting quantum dot (in a 2-DEG, controlled by a voltage through depletion effects) to a superconductor. Such experiments show the quantized conductance characteristic of conduction channels, but the plateaus do not occur exactly at the  $2e^2/h$  values expected for a semiconductor, or at  $4e^2/h$  expected for a superconductor (involving Cooper pairs). Instead, the value (for a specific set of conditions measured as an example) is  $2.2e^2/h$ , which may be interpreted as a transmission probability of 0.85.

Under study at Delft is a shallow 2-DEG which has been prepared 30 nm below the surface (prepared in Glasgow). These experiments will attempt to observe coherence between the s-n-s regions of the devices to be fabricated. Researchers there hope to observe superconducting-induced effects in semiconductors.

Anticipated experiments at Delft involve contacts to InAs sandwiched between InP layers. The virtue of InAs is that the band-bending at the surface is such as to attract carriers to the surface rather than to deplete carriers at the surface, as is the case with many other semiconductors. Thus, if metal contacts are made with the InAs material directly at either end of a 2-DEG of InAs heterojunction material, there is a good chance that the superconductor carrier injection will carry directly into the 2-DEG with more efficient transmission through the semiconducting area of an s-n-s junction.

The superconductor-semiconductor interface is also under study at Groningen. Advantage is taken of the surface structure of InAs to obtain a Schottky barrier that will pass current from a superconductor to a 2-DEG. Since the InAs band-bending is such as to give an enhanced carrier concentration at the surface, this material is being used with GaSb as the quantum well and for contacts with the superconductor. The device under examination currently is simply the 2-DEG with niobium couplings on either side: an s-n-s configuration. It is clear at levels of a few microvolts that the I-V curve for the device shows a supercurrent, where the slope approaches infinity for current values of up to 10  $\mu$ A. With this success, experimental configurations are being fabricated with hopes to observe quantized conductance in the supercurrent.

### 3.2.13.2 Artificial Grain Boundary Junctions

Junctions with YCBO have been fabricated by cutting the substrate material (e.g., strontium titanate) and "re-gluing" the grain boundaries with mirror image symmetry [131]. This produces a "weak link" for the YCBO grown on the strontium titanate surface (introduced at IBM in 1988). If the coupling is "just right," JJ effects are observed. The critical current density is highly dependent on the angle of the crystalline planes at the interface, with a low value for 45° angles and some 20 KA/cm<sup>2</sup> for 32° angles. Good reproducibility of these effects is observed from one sample to the next.

Cavity resonances are observed along these weak link junctions at Chalmers University, Göteborg. Resonances were observed at 256 to 638 GHz from which the London penetration depth and the boundary dielectric thickness are obtained for the sample. The Landau length of 120 to 140 nm is also found [132].

### 3.2.13.3 Two-Dimensional Arrays of Josephson Junctions

A grid of Josephson Junctions is fabricated in a square lattice array, where each "arm" of a square region in this array consists of a JJ made of aluminum-aluminum oxide-aluminum. The size of this array is on the order of 100 × 100 (overall 20,000 junctions). In a magnetic field at temperatures of 10 mK, charge carriers behave in a manner described by two extreme regions: a) where the orbital motion in each square is clearly defined, and the JJ barrier is low relative to the magnetic levels defined; and b) where the orbital motion is inhibited relative to the charging energy  $e^2/2C$  across the junction. Under conditions of region a, the I-V relationship is one of a superconductor, with the slope of the curve approaching infinity at zero applied voltage across the array. Under conditions of region b, the I-V relationship is one of a semiconductor, with the slope of the curve approaching zero at zero applied voltage. The behavior of this system with charges in the grid regions induced with a gate voltage should demonstrate a quantum Hall effect. The fabrication of such a device has not been easy, however. Experiments are under way at Delft to fabricate a gold plate over a silica insulator on a 180 × 60 array to demonstrate these effects.

Two-dimensional arrays of superconducting junctions are under study at Chalmers University, Göteborg, Sweden. By changing film thickness in these arrays, a wide range of behavior relating array resistance as a function of temperature may be obtained. Most impressive is the change of resistance by five orders of magnitude with a magnetic field of a few gauss (at temperatures of 15 mK). According to opinions offered here, such a device is more sensitive than a SQUID. If such an array were to be constructed from high temperature superconducting materials, it should demonstrate the same effect at higher temperatures.

The theory of the behavior of superconducting junctions is known as the "Orthodox Theory," and was developed by Likharev and Zorin in 1985. This involves the postulate that current and flux are conjugate noncommuting variables. Experiments to test this theory continue at Chalmers to verify consistency with the Orthodox Theory.

### 3.2.13.4 Superconducting Field-Effect Transistors

The challenge of fabricating a device in which the conduction across a channel of a superconducting device may be controlled with a gate is underway [133]. Materials involving gold, strontium titanate, and copper strontium copper oxide are being fabricated in layers to fabricate this structure. It is anticipated that under the proper conditions, such control will be possible. Effects have been observed in which the resistance as a function of temperature for a superconducting bridge may be changed by "approximately one degree Kelvin" by the application of 1 V on a gate.

### 3.2.14 Models for Transport through Devices

A variety of theoretical problems associated with important experimental results or anticipated experiments are being undertaken at the Walter Schottky Institute, Garching. A new method of solving the Boltzmann Transport equation has been introduced by using a cellular automata method (borrowed from relatively new methods in fluid dynamics). This method removes the coupling between the position and momentum in these equations. It is faster by a factor of 100 compared with Monte Carlo methods. With this modeling technique, domain formation and noise effects in transport behavior may be obtained. It is also possible to show how doping profiles, alloying, etc. may improve the current-voltage relationships of devices (such as IMPATT diodes).

Modeling the transport of carriers through complex geometries represents a challenging mathematical problem. This is especially true in three dimensions where the grid necessary to predict the behavior in complex geometries results in huge numbers of calculations. Large scale parallel processors are being introduced at Glasgow to solve these problems [134-138].

Two main methods for solving these problems are being exercised at Glasgow. First, the Monte Carlo method is easy in concept, but may not truly represent the behavior due to the difficulty in accounting for correlation effects between and among charge carriers. Second, the fluid dynamics model of carrier flow in a complex geometry is simulated. For these models it is found that the mathematics of quantum effects for transport in these devices has been developed in the field of traffic theory, now termed "Quantum Traffic Theory." Solving the problems of traffic flow in cities is isomorphic with this quantum mechanical problem consisting of nonlinear complex stochastic systems. Ultimately a model is to be developed that includes prediction of the properties of silicon in conjunction with the six-dimensional solution to the equations describing the system. This will require huge parallel computational systems.

### 3.2.15 Lattice Strain and Light Emission

Some calculations have also been made at Garching regarding the possibility of making group IV light emitters. Germanium, for example, with a tin dopant might give a direct band gap. Lateral strain is needed to achieve this. This could be obtained with one layer of tin every 10 to 20 layers of germanium. In silicon, some 12 percent of uniform strain is needed to obtain a direct band gap; this is considered too much to achieve experimentally. However, it is predicted that 2-D silicon will be a direct band gap material. Other calculations indicate the behavior of a regular superlattice under the appropriate conditions. In carefully applied electric fields, it seems possible to obtain Bloch oscillators at terahertz frequencies. The barrier heights, spacings, and fields must be carefully matched to achieve such action. Competing relaxation effects must also be controlled to keep from expending imparted energy into alternative nonproductive channels involving energy dissipation.

### 3.2.16 Statistical Fluctuations

As nanostructure devices become smaller, the inevitable statistical fluctuations of either impurity states or atomic numbers become more important. This leads to the breakdown of the approximation that the material is a continuum, with consequent complexities in transport phenomena. Several efforts at Glasgow are revealing information about the nature of such properties.

The voltage-current relationship of a necked-down portion of a simple conductor shows a complex sequence of extrema due to the boundary conditions that must be satisfied. Introducing a dopant in a semiconductor leads to still further complexities, as the dimensions of the conductor are such that a fluctuating number of dopant atoms appear as a granularity throughout the sample neck [139]. This

random nature is simulated with models in which the potential function fluctuates in a random manner. The model predicts behavior similar to observations for these devices. While, of course, it is seldom possible to observe the actual distribution of donors in a doped sample, nevertheless the fluctuations observed from one device to another may be predicted with the models developed in this case.

It is even possible to extract information about the random location of donors from the mobility of the charge carriers observed. Electrons are much more sensitive to random fluctuations in one-dimensional conductors than in a two-dimensional gas. This is interpreted as a profusion of alternate channels for the charge carriers in the 2-DEG that effectively provide alternative channels for low barriers to conduction.

Another conclusion that may be drawn from the modeling efforts along these lines is that the distribution of electrons among donor atoms is less than random. This is true because of the electron-electron repulsion effects. As the electrons populate donor atoms located randomly, those donor atoms that are close together are less likely to be populated due to this repulsion. The fluctuations in potential energy are thus less than a model in which electrons choose each donor atom at random.

The Shubnikov-de Haas effect has been recognized for years as a sequence of oscillations in the transport properties of a semiconductor as a magnetic field is increased. The population of the sequence of Landau levels produces an alternation as the levels are populated at the Fermi level. Fluctuations in the potential energy of a sample due to random fluctuations in donor location produce locally varying conditions for satisfying the oscillations. This results in a damped sequence of oscillations as compared to predictions for ideal materials. The damping of these oscillations is modelled in a manner similar to the above models for conduction; the results allow the experimental observations to be understood in terms of the fluctuating donor concentrations due to atomic granularity. These results are also being correlated with magnetocapacitance measurements at Glasgow.

These models are being extended to a large number of devices and measurements. Noise characteristics of resonant tunneling diodes are under study at Glasgow (excess noise due to quantum mechanical tunneling adds to the shot noise present). There is ample reason to understand the noise sources and fluctuations in device behavior due to the inherent granularity of materials at the nanometer level.

### *3.2.17 Thermoelectric Effects*

Voltages produced by small thermal gradients (thermoelectric effects) have received only minimal attention in the literature [140-143]. It is felt, after looking at the magnitude of these thermoelectric effects, that they will be the limiting source of noise in nanometer devices. It is clear that these small devices will generate heat causing thermal gradients. The magnitude of the noise thus produced will tend to dominate the stochastic nature of signals passed through such devices. Additional investigations in this area involve quantized thermal and thermoelectric effects in Aharonov-Bohm rings, quantum point contacts, and periodically modulated structures.

### *3.2.18 Phonon Behavior*

#### **3.2.18.1 Phonon Structure**

A Nottingham program attracting recent attention involves observations of the phonon structure in 2-DEGs shortly after a transient thermal impulse (laser pulse). By scanning the area that has been pulsed with a raster scan from a second laser, and observing the image in the reflection coefficient of the scanning laser, surprisingly detailed pictures can be obtained of the phonon structure that has been excited. The structure observed by this method exhibits striking anisotropies arising from momentum and energy



conservation. Information about the frequency spectrum of the phonons emitted and the thermal relaxation behavior of the electron gas are being elucidated with these studies.

The fundamental relationship between energy and wave vector for these phonon structures is not well understood. By analyzing these images as a function of time the dispersion relationships may be determined. The research at Nottingham is determining experimentally for the first time the relationship that has been calculated theoretically some eight years ago by Feynmann. It is anticipated that this work will appear in *Physics Review Letters*.

### 3.2.18.2 Isotopically Pure Ge and Ge Phonons

The purchase by the U.S. (in Berkeley) from Russia of some isotopically pure elements has allowed an opportunity to examine some unusual characteristics and fabrication methods involving germanium at the Walter Schottky Institute in Garching. The phonon structure of germanium is a critical ingredient related to carrier relaxation in transport properties. This phonon structure is gaining increased scrutiny by growing isotopically pure atomic steps of germanium, with 2, 4, ... 24 atomic layers of  $^{70}\text{Ge}$  alternating with  $^{74}\text{Ge}$ . A diagnostic phonon line (Raman spectra) in isotopically mixed Ge is sharp and at a frequency represented by an average mass [144]. With isotopically "stepped" Ge with a large number of atomic steps ( $>20$ ) of the 70 isotope alternated with the 74 isotope, two phonon lines are observed representing the mass of each isotope. This is an "isotope superlattice." When the number of atomic steps in each layer is less, the phonon structure appears that clearly mixes the vibrational lattice modes. This is a beautiful demonstration of the admixture of the quantized levels of the two separate phonon structures in each isotopically pure subset.

It also happens that the transmutation of  $^{70}\text{Ge} + \text{neutron}$  results in gallium, whereas that of  $^{74}\text{Ge}$  results in As. It is therefore possible to irradiate (in a neutron chamber) selected patterns of isotopically pure Ge to obtain Ge doped with Ga or As. By this method, the steps of the n- and p- doped levels can be made exceptionally sharp.

An additional feature of  $^{73}\text{Ge}$  is a very sharp (one part in  $10^{10}$ !) resonance at 13.3 keV. By alternating isotopically pure  $^{73}\text{Ge}$  in a matrix of  $^{70}\text{Ge}$ , a Fabrey Perot structure at this energy should be possible. Experiments are anticipated to characterize the ability to monochromatize the synchrotron X-ray radiation at 13.3 keV with this unusual material property.

### 3.2.18.3 Phonon Transport

Experiments attempting to measure thermal conductivity involving phonon transport were described at Cavendish Laboratory [145-149]. Such measurements are difficult because in most materials the thermal transport appears to be dominated by electron carriers. The experiment involved doped single crystal semiconductors of GaAs (doped with  $10^{17} \text{ Si/cm}^3$ ) that were fabricated in parallel stripes along the (001), (111), (221) planes. Free-standing triangular wires were fabricated with dimensions of  $0.4 \mu\text{m}$  wide by  $40 \mu\text{m}$  long. The thermal conductivity of these wires were dominated by metallic conduction mechanisms even at 0.3 K, but it was observed that at temperatures below 1 K the hopping length changed from a characteristic 3-dimensions to 1-dimension (and a length of  $0.5 \mu\text{m}$ ) indicating that wall effects begin to dominate the relaxation mechanism.

### 3.2.19 Biological Behavior

The laboratory at the University of Glasgow has been developing techniques to guide biological cell growth with lithographic modifications of base structures. Several years ago they demonstrated the ability



to measure voltages emitted by cells grown along predetermined paths [150-153]. They formed a cross grid of platinized electrodes covered with silicon nitride into which grooves had been etched (to the depth of the platinum). Heart cells were placed in these grooves and cell growth proceeded along the grooves. The beating of the heart cells was observed with a clear temperature dependence of the frequency upon temperature and health of the nurturing solution. Variations such as measuring the voltage emissions from cells with electrodes "impaled" in the cell gave significantly different behavior. Cells transmit signals more slowly once they are impaled.

### 3.3 Quantum Dots

General review articles addressing the properties of nanodimensional particles may be readily found [154]. of particular interest are the optical properties that reveal confinement effects and interactions with neighbors. More recently there has been considerable interest expressed in exceptionally narrow spectral luminescence observed from a single quantum dot at low temperatures. This suggests that an ensemble of quantum dots all having the same size may exhibit interesting bulk properties.

#### 3.3.1 *Near-Field Optical Microscopy on Quantum Well Structures*

A near-field optical microscope has been constructed at Walter Schottky Institute, Garching, using an aluminum coated silica fiber. With this probe, 50 nm resolution may be obtained [155]. This probe may be used to expose a resist, although the near field pattern spreads out rapidly (experiments performed at Garching indicate that the width of the near-field pattern is at least a factor of two wider than the "optical orifice" a distance away from the probe equal to the width of the orifice).

This probe offers new opportunities to examine spatial variations of photocurrents, local structures within two-dimensional conduction channels, and spectroscopy to identify local structures.

Looking at AlGaAs quantum well structures, it is possible to detect the photoluminescence with this optical probe. Typically the width of the spectral line is 3 to 4 meV at 1670 meV energy (for the frequency of the spectral line center). While observing this photoluminescence at 4 K, interesting spectral structure was observed, including several satellite lines of an initially unexplained origin. Experimentation revealed that the satellite pattern shifted with the spatial position of the probe on the sample. A two-dimensional x-y plot of the appearance of specific satellite lines shows their spatial distribution at certain well-defined positions on the heterostructure (lateral resolution of 1.5  $\mu\text{m}$ ). Further, the shift of the satellite structure from the main luminescence line appeared to be correlated with the size of a quantum dot associated with each occurrence on an x-y grid. The identification of these satellites is thus understood in terms of bulges in the 2-DEG. These bulges produce quantum dot behavior in the luminescence, and a confinement shift depending on the size of the bulge. The sizes of these bulges (quantum dots) are on the order of 300 Å.

By experimenting with the power dependence of the luminescence of these quantum dots, saturation was observed. With the appearance of this saturation was the simultaneous appearance of two luminescence peaks at higher and lower wavelengths. The interpretation of this behavior is that the nonlinear absorption results from a coherently excited 2-photon process yielding two excitons. The 2-photon absorption process is much narrower than the normal 1-photon process (30 micro-eV out of 1656 meV). This effect can be seen in the absorption from linearly polarized light (one right-handed, one left-handed circularly polarized photon) but not in circularly polarized light.

### 3.3.2 Capacitance Spectra of Quantum Dots

The capacitance of an array of quantum dots between two plates is measured as a function of a ramp voltage between the two plates at the University of Munich. As the ramp voltage is increased, successive numbers of electrons populate the quantum dots. This is seen as steps in the out-of-phase portion of the dielectric constant of the array as each successive electron is placed on the quantum dot. The uniformity of the dimensions of the quantum dots is critical here.

### 3.3.3 Luminescence and Lasing Properties

Quantum dots are fabricated at the Technische Universität Berlin by growing 1 Å layers of InAs/GaAs using MBE methods. The quantum dots appear due to a slight lattice mismatch between the two materials. To relieve the strain, alternate centers of higher concentration are formed (bunching of the atoms in a thin layer), providing the basis for the formation of quantum dots. The dynamics of this material formation is basically a balance between cohesive and adhesive forces, and can be monitored in the RHEED pattern during growth. Once this layer of quantum dots is formed from a 12 Å InAs/GaAs pattern, an additional 7 nm layer of GaAs is overgrown. The product is a pattern of well-shaped quantum dots 12 nm in dimension with a 20 percent dispersion in size.

Luminescence of these structures with a maximum at 1.1 eV has a width of 0.06 eV. The wavelength of maximum luminescence shifts with changing dimensions (obtained through a change in processing conditions). The width is limited by the polydispersity of the sample.

A most interesting spectral pattern is obtained by looking at a very small portion of the sample at the "high energy side" of the sample. With 42 nm spatial resolution, this "wing" of the spectrum is actually probing a very small number of particles [156]. The spectrum is very complex, with a large number of extrema. This complexity is due to the fact that each quantum dot is actually being observed, and the shift from one dot to the next is due to the different size of each dot in the polydisperse sample. Each spectral peak due to a single quantum dot has a 0.17 nm line width at a wave length of 880 nm (which is the spectral resolution of the instrument). It is felt that neighboring peaks in the complex spectrum are due to quantum dots that differ by one InAs molecule in number (i.e., 4000 atoms for one peak, 4001 atoms for the next, etc.). This behavior seems to suggest that the spectral purity of a truly monodisperse sample of quantum dots could exhibit a most interesting strong and very narrow absorption peak.

Quantum dot lasers have been fabricated with this material [157]. Electroluminescent excitation and lasing of the quantum dots takes place at 77 K with thresholds of 120 A/cm<sup>2</sup>. An additional advantage of lasers fabricated from quantum dots is that the chirp and temperature dependence should be minimized due to the narrow density of states. Such lasers should also be capable of supporting high band widths for communication purposes.

Photoluminescence and cathodoluminescence has been used at the University of Lund, Sweden to excite InP imbedded between layers of GaInP [158] and GaInAs [159]. In addition, STM has been used to excite some of these materials [160]. The strained InP layer with approximately 10 monolayers of thickness spontaneously reforms into quantum dot structures with lateral dimensions of 100 nm. These quantum dots luminesce when excited with STM probes (luminescence at 1.6 to 1.85 eV). Investigations here have demonstrated line widths of less than 0.1 meV at 77 K.

### 3.4 Quantum Wires or Pillars

#### 3.4.1 *Quantum Wires of GaAs*

A self-assembled method of growing quantum wires of GaAs was found accidentally during the growth of AlGaAs on structured surfaces [161-163]. In the process of growing AlGaAs on lithographically etched surfaces, the different sticking coefficient and the mobility of surface atoms during crystal growth result in a concentration buildup of GaAs at the intersection of certain facets of AlGaAs. This is in effect a quantum well of GaAs surrounded by the higher band gap of AlGaAs. The dimensions of these quantum wires are roughly 5 nm in the lateral direction and 100  $\mu\text{m}$  along the long axis. The luminescence shows a blue shift, although some show a red shift that is not entirely understood [164]. Fabrication and characterization of an array of quantum wires by this method shows a uniform dimension along the length of the wire as well as from one wire to another on the same AlGaAs base. The spectral line widths do not seem to significantly broaden, indicating the uniformity of the dimensions of these structures. Earlier work on luminescence from SiGe wires [165] has been preliminary to the work with GaAs.

The (311)A surface of GaAs undergoes a reconstruction resulting in surface features with a 32 Å period and a depth of surface "furrows" of 3 Å [166]. This has been seen by STM and Reflection High Energy Electron Diffraction (RHEED) patterns. An effort at the Paul Drude Institute, Berlin involves observing the anisotropy of photoluminescence and transport properties associated with AlAs, Ga, or Si deposited on this surface, and hence taking up the quantum wire geometry as the "surface furrows" are filled with a second material. The behavior of the monolayers grown on this surface is revealed in considerable detail, with layer depth, dangling bond density, etc. observed or calculated from experimental observations.

Additional self-organized growth of quantum wires has been demonstrated by growth of silicon atoms on the GaAs(001) vicinal surface [167]. Raman scattering has characterized the silicon incorporated on this surface, indicating substitution of the silicon on Ga sites. A pronounced polarization asymmetry in the Raman scattering intensity was observed suggesting the "wire" aspect of the silicon atoms aligned in a chain-like fashion at the surface.

Instrumentation associated with this effort includes MBE, STM (samples transferable from MBE to STM under vacuum), RHEED, Photoluminescence, Raman scattering, and ellipsometry [168]. An interesting aspect of crossed-beam ellipsometry was pointed out: this technique is able to detect surface reconstruction and monolayer sensitivity by observing difference spectra along the two polarization angles).

#### 3.4.2 *Quantum Wires in "V-Groove"*

A number of attempts to prepare quantum wires on vicinal surfaces have indicated the difficulty of preparing uniform structures by this method. The samples always seem to have a dispersion of sample lengths and kinks in the wire structure. Research at the Technische Universität Berlin has undertaken efforts in conjunction with former efforts at Bellcore (in the U.S.) to fabricate quantum wires by growing approximately 8 nm of GaAs in "V-grooves" of AlGaAs [169]. The structures fabricated in this manner are quite uniform, and are shaped with the majority of the GaAs at the sharp tip of the groove (with a small amount extending along the sides). Size fluctuations of a sample prepared in this manner are small, and the uniformity of sample dimensions and properties is good.

The sub-band structure can be observed for these quantum dots, in which two to three sub-bands can be resolved in luminescence spectra (depending on temperature). The width of these spectral lines is

approximately 5 percent at the 710 nm fluorescence peak. Laser thresholds of less than one mA (100 to 200 A/cm<sup>2</sup>) have been observed with these quantum wire structures.

Modeling of the bound states that should be observed for these quantum wires uses the solution of the wave equation in these unusual geometries [170]. In addition to geometry, additional parameters that must be accounted for to understand the behavior include lattice strain caused by the piezoelectric nature of the sample, many-particle interaction, and coulomb interaction forces.

Interesting "Type II" V-groove quantum wires are under conditions in which InAlAs/InP junctions are grown in the presence of a V-Groove geometry between the two materials. Solution of Poisson's equation suggests that, at the tip of the groove, due to the band offset at the heterojunction, there should be a minimum of potential energy in the conduction band for charge carriers. This, then, becomes a quantum wire due to the geometry and band offset alone, with no requirement that the material be deposited to a precise depth. Such a "natural appearance" of quantum wires is being sought for future studies.

#### 3.4.3 *Quantum Wires by Interdigitated Fingers*

A number of the efforts at the University of Munich concentrate on electrically tunable optically active devices. The advantage of tunability results in increased frequency flexibility in working with any conceived system.

Quantum wires may be induced by placing a voltage on a sequence of interdigitated fingers [171-174]. The alternating fields are reflected in a modulation of the conduction and valence bands, a structure that resembles a lateral "nipi" structure in solid state physics. As the conduction band dips down to the Fermi level, conducting channels are populated at these dips, resulting in an effective quantum wire along each finger. The height of the barrier can be tuned by voltage, the Fermi level can be modified with a back voltage, and the distance between interdigitated fingers may be varied by fabrication. This system represents a flexible means of changing the population of carriers in the quantum wires. This result is a tunable wavelength and a great deal of flexibility in the overall parameters characterizing these devices. As is the case for all electromagnetic systems limited by the population of energy levels, these devices work well below temperatures of  $kT$ , which, for these cases, is less than 1 K.

#### 3.4.4 *Quantum Wires (Growth and Luminescence)*

Quantum wires were fabricated by clever partial undercutting of a resist on a GaAs layer that had been placed over an AlGaAs layer, all on a GaAs base [175, 176]. These wires have also been fabricated for InP on InGaAs [177]. Wet etching is used at the University of Würzburg to avoid damage to sidewalls, and is seen to be "a fairly reliable process." As far as obtaining good quality control, the resist is patterned to take into account the amount of undercutting expected from the wet etching. One claim suggested that there had been no reliable work done on quantum wires produced by dry etching due to the problems with damage to the surface. Researchers at Würzburg have found that 40 nm wires produced by dry etching had totally quenched some photoluminescence effects, a phenomenon explained by the depth of damage due to the dry etch process. Some consideration might be given to performing chemistry in a dry etching process without ionization where such damage is minimized; some groups are doing this, for example, at IBM and AT&T.

Quantum wires of InGaAs produced on InP by this method demonstrate good confinement shifts in complete agreement with particle in the well predictions [178-180]. Shifts from 0.90 eV to 0.96 eV with line widths of 9 nm (out of 1300 to 1400 nm) were obtained. Additional emission is observed from higher

states consisting of the sub-bands. These emissions are observed with increasing power at temperatures of 2 K.

The polarization of the photoluminescence (PL) spectra of these quantum wires was measured at the University of Würzburg. As the wire becomes smaller and smaller, a greater degree of polarization difference is noted, with the plane of polarization perpendicular to the long wire axis down to 20 percent of the emission intensity along the wire axis. This variation is explained simply as due to the geometry of the particle and the consequent difference in depolarization along each axis.

In addition to the PL spectra obtained on wires, quantum dots of 30 nm dimensions were examined at temperatures of 2 K. Sub-band structure was also observed at increasing power levels for these systems.

Magnetic effects were observed in the PL spectra at 2 K. An interesting transition was seen as a sub-band structure transition from zero field into Landau levels at higher fields. A one-to-one correspondence was seen for each sub-band to each Landau level. In quantum dots, the application of magnetic fields demonstrate splittings due to the loss of degeneracy for the two orbital directions of the electrons in the magnetic field.

#### 3.4.5 Luminescence of Single Atomic Impurities in a Quantum Wire

GaAs/AlGaAs structures may be prepared with laser interference patterns to produce lateral patterns mimicking the interference pattern. By subsequent etching and growth, parallel V-grooves are prepared in which accumulated GaAs (at the tip of V-grooves) form quantum wires. With a few monolayers-growth of GaAs, these wires are terminated into short wires with aspect ratios of 2:1 to 10:1. A sample with about  $10^{15}$  carbon atoms/cm<sup>3</sup> has a good probability of finding one (or a few) such impurity atoms acting as acceptor states in a single quantum wire. Cathodoluminescence (CL) experiments demonstrate the luminescence of a number of quantum wires in which one (or a few) such carbon atoms are found [181]. Identification of the occurrence of a carbon impurity is by the spectral shift from 1.62 to 1.54 eV in the luminescence.

#### 3.4.6 Pillars from Aerosol Particle Templates

Columnar pillars may be fabricated by etching a surface on which nanometer-sized particles rest. The small particles serve as a mask to the etching process, forming columns under each particle. This technique has been used for several years by various researchers, but suffers from the fact that aerosol particles are generally produced with a distribution of sizes, and even shapes.

In order to obtain monodispersivity of the aerosol sample at Lund, Sweden, the sample (in a carrier gas) is passed through 1) a charged region to deposit a single charge on the aerosol particles, and 2) a differential mobility analyzer, in which an electric field is passed from a center wire to a surrounding cylinder [182]. The charged aerosol particles migrate from the center to the cylinder wall with rates depending on the aerosol sample size. An annular ring collector passes a relatively monodisperse aerosol sample. The diameter of the sample produced in this manner varies by about 1 to 2 percent, a substantial improvement in samples produced by most other means. Sintering of the particles subsequent to size separation produces a greater uniformity of shapes in addition. By allowing the aerosol particles to settle onto a surface, particle densities approximating  $10^{19}$ /cm<sup>2</sup> may be obtained in a 10 minute period.

Columnar pillars of InP have been produced having diameters of 20 to 80 nm (monodisperse, with variations among different samples depending on conditions) [183-185]. Sample lengths are typically two to three times the sample diameter. Low-temperature cathodoluminescence has been used to characterize

these structures. The spectral line widths of these samples at 25 K are 0.01 to 0.02 eV at 0.9 eV center emission [186]. Overgrowth of the InP on GaInAs produces the narrower line widths.

An AFM tip was used to observe these samples. It became clear that the radius of curvature of the columns was smaller than that of the AFM probe, and that each column appeared in the image produced with the shape of the silicon nitride AFM tip. A consequence of this observation is the proposal that by depositing a molecular structure on the AFM tip and imaging with these columnar structures, the topography of the molecule might be obtained with an "inverse" approach to imaging small samples [187].

### 3.4.7 Luminescence from Silicon

The mechanism involving luminescence from "porous silicon" is being addressed at the Technische Universität in Munich. Pillars of silicon have been produced 5 nm in diameter and 40 nm in height [188]. This was done by lithographically depositing 5 nm dots of gold in regular arrays. Directional etching leaves the silicon pillars with small amounts of gold at the tip of each. The group intends to apply a voltage to these pillars to see if the luminescence may be excited with electrical current.

#### 3.4.7.1 Porous Silicon: Detailed Observations at the Universität of Munich

Extensive work is being conducted with the various measurements attempting to understand the luminescent mechanism in porous silicon. A number of different observations have been made at the Technical University at Munich, each providing additional information about this puzzle.

One such measurement involves the direct transport properties across a Schottky barrier in which metal is deposited directly on porous silicon, with p-doped silicon as the other electrode. Rectifier behavior is observed in the I-V curve. This has been examined for different thicknesses of porous silicon to conclude that the porous silicon is merely acting as a resistor and does not contribute to the rectifying behavior (the diode is due to the interface between silicon and the porous silicon with an activation energy of 0.5 eV).

The dependence of conductivity upon frequency [189] demonstrates a relatively insensitive dependence at higher temperatures, leading to the conclusion that the conduction mechanism is one of hopping rather than energy activation, as is the usual semiconductor transport mechanism. There appear to be transitions between energy levels at higher frequencies, effectively giving a hopping mechanism.

The resistance of porous silicon is voltage dependent. This behavior is attributed to a Poole-Frenkel type of mechanism [190]. Unusual discontinuities have been observed in the I-V curve at low voltages, with slopes approaching infinity under some circumstances. This behavior has been determined to be due to the breakdown of gas between various positions in the porous silicon, when the field is sufficiently high at selected points in the tangle of fingers in the material.

Measurements involving photocurrent as a function of photon energy have revealed discontinuities in this relationship at approximately 1.05 eV. This is interpreted as due to band-bending inside the porous silicon.

It is concluded in these studies that the presence of hydrogen is not necessary for the porous silicon to luminesce.

The etching intensity results in a change in the lifetime of the luminescence, by as much as a factor of ten. Smaller particle size results in a shorter lifetime. The lifetime shifts with temperature of the sample.



The lifetime at room temperature is dominated by mechanisms that are non-radiative. The lifetime of the luminescence appears to decrease with shorter wavelength emission over 1-1/2 orders of magnitude.

There are actually two emission wavelengths from porous silicon. One of these is the usual emission in the red. A second emission appears in the blue region of the spectrum. Careful oxidation of porous silicon at higher temperatures gives a higher percentage of the blue emission. At 1100° C, the emission is all blue.

Another consideration that could be responsible for the shift of the emission wavelength is that of shear forces due to an oxide on silicon. Such considerations are under investigation.

Electron Paramagnetic Resonance (EPR) observations have revealed a 12 gauss line width. There is an inverse relationship between spin density and luminescent intensity over three orders of magnitude. It is concluded from this that there are near-neighbor interactions resulting in this broadening and possible quench mechanisms.

It has been concluded that there are at least two non-radiative mechanisms and one radiative mechanism.

These observations seem to point to three principal parameters that are critical to understanding what is happening with this material. These parameters are: 1) size of the particles in the sample; 2) stress on the sample; and 3) the presence of oxide on the sample.

One model that could explain many of these observations is that of an electron-hole pair that has been localized near the surface. Surface stress would therefore play a significant role in the blue shift that has been observed in some circumstances.

All of these observations have been directed at understanding the injection and transport mechanisms in porous silicon. It is only with such systematic and varied observations such as these that such a confusing and complicated system such as porous silicon will be understood and the limitations of its utility revealed.

#### **3.4.7.2 Porous Silicon at Philips Laboratory**

Porous silicon has been under study at Philips Laboratory. The fundamental question driving the research directions here relates to the ultimate efficiency that may be available from porous silicon. If the ultimate efficiency were likely to be high, it could become industrially important; if not, it would not be an item of interest.

Careful measurements involving transport across silicon/porous silicon/metal (Schottky barrier) structures were made. The behavior of this sample resembles that of a diode in series with a resistor. A plot of the log (current) vs voltage for a number of metals contacting the porous silicon gives a number of curves all overlapping with the same slope and value at low voltages. At higher voltages the "saturation current" is different for each. A conclusion from these measurements is that the current across this fabricated sample is not limited by the Schottky barrier since the "prefactor" in the equivalent circuit turns out to be the same for all metals investigated (with one exception that formed a poor contact).

A second set of experiments involved observations of the photocurrent produced by shining light onto the sample with a one-micron spot as the location of the spot is moved from the metal junction to the silicon end. The photocurrent observed is a sharp peak when light is shined on the silicon end of the sample. A conclusion reached is that the diode behavior of the sample is due to hole injection.



From these measurements, it is concluded that porous silicon has an intrinsic wide gap. Band bending at the interface gives the observed photocurrent, which is limited by hole injection at the substrate. If the band gap were wider due to confinement effects (originally postulated when this effect was observed) then a different band gap would be observed than these observations suggest.

The conclusion is that it will be very difficult to make an efficient electroluminescent device since it's hard to inject carriers into a region of greater band gap (which presumably the confinement region of the porous silicon would have). Hence further research into this material is not anticipated at this laboratory unless or until this picture appears to be incorrect.

#### 3.4.7.3 Porous Silicon at IBM Zürich

Observations at IBM, Zürich have obtained nanometer-resolution of visible light emission from porous silicon excited with an STM tip [191]. In these experiments there are indications that individual confinement centers have been observed.

### 3.5 Magnetic Materials

Effects associated with giant magnetoresistance have been studied at Philips Laboratory for some time [192-198]. Utility associated with this effect has been recognized industrially with the increased sensitivity available for sensing heads above magnetic storage devices.

The current research at Philips involves the measurement of resistance changes associated with layers of magnetic materials, but a difference in this research is that the magnetoresistance is being measured in a direction perpendicular to the planes. The effects in this direction are of interest due to the markedly different environment through which electrons pass in this direction (alternating spin directions every few atomic layers). However, since the spin-flip diffusion length is on the order of 1000 Å, many layers may be traversed before the diffusion relaxation mechanism is dominant.

These experiments are particularly difficult for several reasons: 1) the sample length is inherently very short (across several deposited metal layers each having a thickness fractions of a micron), and 2) the fields produced are inhomogeneous. Thus the effects due to inhomogeneities in the fields must be backed out of the measurements in order to obtain the intrinsic properties of the material.

The results of these four probe measurements give the change in resistance at saturation and zero magnetic fields and may be compared with measurements made previously in the parallel configuration. For FeCr material, the parallel resistance at room temperature changes by 7 percent, whereas for the perpendicular direction (measured here) it is 15 percent. For CoCu the resistance change at room temperature is 20 percent for parallel resistance and 60 percent for perpendicular resistance. For CoCu at low temperatures it is 40 percent for the parallel direction and 100 percent in the perpendicular direction. This study serves as a model for future measurements and material characterization of these unusual and industrially important materials.

Programs at IBM, Zürich involve the use of local probes for examining magnetic effects. This includes spin-polarized scanning electron microscopy [199] by measuring magnetic forces during scanning. This procedure is used to obtain magnetic domain structure [200, 201] and temperature dependence [202] with a resolution of approximately 40 nm.

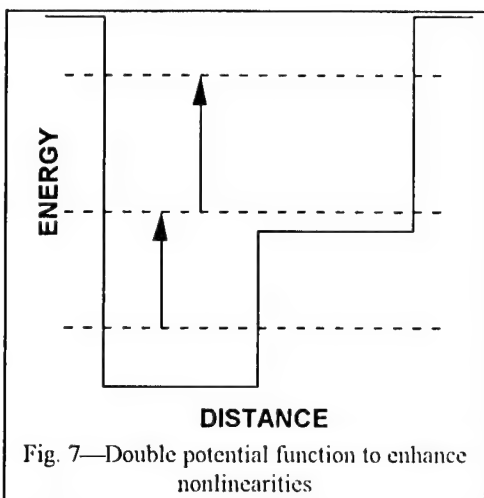
The circular polarization of fluorescence emitted during electron excitation by a tunneling tip provides information about coupling between the photon polarization and the spin polarization of the valence bands

of a ferromagnetic material [203]. The action of a spin polarized electron emitted from a ferromagnetic tip into GaAs has been observed [204]. From these spin-polarized spectral features the local surface density of states of the ferromagnetic material may be probed [205].

### 3.5.1 Magnetic Effects In Nanodimensional Loops

The Aharonov-Bohm effect results from interference between charge carriers traversing two directions around a ring (compare with a Mach Zender interferometer). This effect is frequently observed as complex oscillations in the current-magnetic field relationship due to the interference of electron carriers on the lower-voltage side of the ring. By ion-implanting manganese in the ring of such a device, with levels of 10 ppm such that the material is paramagnetic, the amplitude of the oscillations is found to decrease significantly at lower magnetic field values [206]. At higher magnetic fields, this behavior transitions to that observed without the magnetic impurities. At low fields the magnetic effect is washed out due to the variations of spin on the charge carriers and a reduction of the carrier coherence length. At higher magnetic fields the impurities align with a consequent coherence and interference effect restored. With chromium implanted instead of manganese, the behavior does not quite fit the calculated values predicted by the population of the magnetic levels. This unexpected deviation from theory remains a research problem.

Small loops exposed to magnetic fields have residual currents associated with them. This effect, referred to as persistent currents, has been examined in a number of laboratories [207]. A careful measurement of the persistent current may be conducted with a SQUID, however the perturbation by the measuring instrument must be carefully avoided. One way to do this is to prepare a geometry involving two rings and a measurement device that mirrors the physical geometry but which is able to measure the asymmetry of currents propagating as persistent currents in the ring. A SQUID with a "figure 8" design is fabricated for this purpose. The difficulties of experimental design and the details of how to perform this measurement to avoid the many pitfalls of measurements at these "infinitesimal levels" is the effort being pursued at CEA in France.



## 3.6 Optical Behavior

### 3.6.1 Nonlinear Optical Materials for Frequency Doubling

The use of double resonance for frequency doubling enhances the nonlinear effect substantially with a consequent improvement in the doubling efficiency for the process. This may be "tuned" by appropriate design of the shape of the quantum well with various dopants and layer widths. For example, an asymmetric quantum well in GaAs/AlGaAs materials that has been designed with this double resonance in mind is illustrated [208] in Fig. 7. The layers are typically 60 Å in width. Such structures have been used for efficient

frequency doubling from 10.6 to 5.3 μm.

### 3.6.2 Other Spectroscopic Characterization of Materials

#### 3.6.2.1 High Spin-Spin Interaction in II-VI Heterojunction Materials

Materials with paramagnetic dopants in II-VI materials show interesting effects in magnetic fields. An example that has been studied several years ago at l'Ecole Normale Supérieure, Paris is that of doping CdTe with Manganese in heterojunction patterns. The presence of Mn gives the CdTe a lower band gap.

When a magnetic field is applied to this material, the exchange interaction of the 5/2 spin of the manganese is very high and appears as an effective magnetic field that is quite different from the external magnetic field. Effective "g" values for the conduction electrons are on the order of several hundred, making significantly enhanced shifts of energy levels observed by optical spectroscopy. Also observed are transitions from the occupation of light holes to heavy holes as the valence band energy levels cross one another in magnetic fields of 3 to 4 Tesla. This corresponds to a crossing of the  $M_J = 1/2$  levels with the  $M_J = 3/2$  levels [209]. These experiments are generally performed at temperatures of 4 K.

### 3.7 Organic Thin Films

In keeping with the original intent of the subject, organic thin films were of interest for a variety of reasons. The following is a fair representation of the activities taking place in Europe on this subject.

#### 3.7.1 Organic Thin Film Transistors

The 1980s saw considerable research activity in the design of conducting polymers. Potential utility for these materials was foreseen in a number of areas, one of which was for electronic purposes. The idea of using these materials for the active conducting component for a transistor occurred to a number of researchers. The first of these was apparently made in Thiais, France [210-216]. The types of organic materials introduced in these "organic transistors" included polyacetylenes, polypyrroles (five-membered rings containing a single nitrogen) [217], and polythiophenes (five-membered rings containing sulfur) [218-224], with many variations involving chain length, side-groups attached, method of depositing film (evaporation, electrolytic growth, spin coating, etc.). The design of these transistors resembled the standard MISFET, with a gate voltage applied through an insulator, typically silica (initially). Current-voltage curves were obtained that characterized these devices, and which soon demonstrated where the utility may be advantageous and where certain limitations were to be found. The carrier mobility for many of these films typically was on the order of  $10^{-7}$  to  $10^{-2}$  cm<sup>2</sup>/volt-second (as compared with approximately 1000 for silicon), and limited any thoughts of high frequency applications. By careful selection of fabrication techniques (such as selection of oligomer chain length) and of gate insulating materials (organic insulators were found to offer advantages) mobilities of somewhat greater than unity were obtained—still shy of semiconductor performance for speed. The advantages for these devices appear to be 1) the ease of preparation (no high vacuum or expensive equipment was needed), 2) the mechanical flexibility of the transistors once they were fabricated, and 3) the potential use of these materials as sensors. Even today there is some activity in which industry is contemplating the advantage of having flexible transistors in plastic credit cards, for example.

During the late 1980s, many combinations of materials were tried at the Laboratoire des Matériaux Moléculaires, Thiais, France. Measurements involving optical characterization (absorption spectra, fluorescence, photoinduced absorbance and bleaching, circular dichroism, electromodulated absorption spectroscopy, probes with plasma surface polaritons, etc.), cyclic voltammetry, X-ray diffraction, and transport characterization gave a wealth of information about the true behavior of these materials.

Emphasis today appears to be toward improved understanding the properties of the "molecular wire" along with introducing ion-specific groups in the polymeric materials. These specialized groups (such as crown ethers) will introduce specific sensitivities to ions or materials for which it has specifically been designed. They become Ion Selective Field Effect Transistors (ISFETs), where the sensor is simultaneously the gate of the transistor.

Along with these efforts, new materials are being prepared and characterized that could provide additional information about the nonlinear optical properties of organic molecules [225]. These nonlinear properties are sensitive to many of the parameters of interest for other electronic effects, such as the narrow gap band structure, chain-chain interactions, etc.

In summary, the laboratory in Thiais, France has provided a number of leading measurements on these organic conducting molecular systems, and continues to do so with variations that have not yet been explored in this complex parameter space.

Molecular materials demonstrating transport properties are under investigation at places like Philips Laboratories to make low performance electronic devices. The fact that polymers can be processed at low temperatures and are flexible give them certain advantages. They may have desirable piezoelectric properties or may be inexpensively fabricated for use on a credit card, where logical operations on the credit card itself are an advantage. The speed of such devices seems to be inevitably slower than that in semiconductors due to the mobility limitations associated with molecular systems. The relatively new area of light emission by molecular systems (polymers) also offers additional incentive to study these materials.

### 3.7.2 *Organic Monolayers for Insulation*

Researchers at Villeneuve, France are investigating organic monolayer properties for use as insulators. The gate insulator for a Si-FET is typically silica. For submicron channel lengths, the dimensions of the silica become on the order of 5 nm. This is almost comparable with some distances achieved by Langmuir-Blodgett films, or even monomolecular layers. Organosilanes or thiols may provide an alternative to this insulating layer [226, 227]. It has been shown [228] that an 18-carbon silane forms an excellent insulating film withstanding dielectric breakdown at fields of 9 to 12 MV/cm. Alkane chain lengths are varied from 8 to 18 carbon units. No dependence of the conductivity upon chain length is found, in contradiction to trends found in Langmuir-Blodgett films measured elsewhere. Explanations for this apparent anomaly are currently being investigated. Additional efforts at this laboratory involve the fabrication of silicon quantum dots by filling holes with silicon, attempting to find luminescence and hence a system that will explain many of the confusing observations associated with porous silicon.

### 3.7.3 *Local Probe Characterization of a Surface Film*

Local probes are beginning to reveal details about surface films that have only been postulated several years ago. Realistic behavior is more complex and revealing about molecular behavior at a surface than originally thought. The details available from these measurements are fascinating, and represent one of the scientific frontiers to understand material interactions.

#### 3.7.3.1 *Structure of Substituted Alkanes at a Surface*

Alkyl derivatives such as thiols (with a S-H group at one end of a hydrocarbon chain) have been examined on a well-formed graphite substrate at temperatures just above the melting point of the thiol (room temperature and above, depending on the substance examined). At these temperatures the molecules

are immobilized on the substrate with well-defined patterns that may be observed with STM [229-237]. The systems are prepared either in the neat melt form or in a solution with a solvent present.

The patterns observed at the Universität Mainz show clear crystalline patterns with the head groups aligned in various patterns. The alignment variations correspond to different two-dimensional phases of the molecules in the graphite environment. Some molecules demonstrate Moire patterns as the natural two-dimensional crystalline spacings of the molecule do not quite match that of the underlying base structure.

At the Universität Mainz diacetylinic linkages have been placed in the middle of hydrocarbon chains with the hope of observing the changing structure upon photolytic polymerization of the two-dimensional crystal with the double bonds adjacent to one another. The polymerized product has not yet been observed in these experiments.

Future experiments at Mainz point to the introduction of increased complexity of the functional groups on the molecular system. Bridging groups and hydrogen bonding groups, for example, will be introduced. Substrate variations using materials such as molybdenum sulfide and molybdenum selenide are being considered. The effect of doping, the nature of the dopant species (whether n-type or p-type), the polarity of the scanning tip, etc. all represent variations that will inevitably broaden our knowledge of these molecular systems and fill in the gaps of how to prepare and characterize the interaction of molecules with surfaces in these "real" environments.

Interestingly enough, molecular dynamic simulations assuming the Leonard-Jones potential gives fairly good models of the type of patterns observed here. The model even predicts the tilting of adjacent molecules, as observed experimentally.

Philips Laboratory in Eindhoven has worked with self-assembled monolayers consisting of aliphatic thiols on gold. Microscopic observations have revealed apparent "holes" in the coatings fabricated. These holes, upon closer inspection with the STM probe, (revealing atomically resolved sulfur atoms; the hydrocarbon chains were not atomically resolved) shows that the holes are really domains with a different two-dimensional structure [238]. In order to see the sulfur resolved at the atomic level it is important to use low tunneling rates (it is not atomically resolved at high tunneling rates). The holes also migrate and disappear at a step edge in the underlying gold structure.

Organic monolayer formation with vacuum-deposited alkyl chains on a gold(111) surface have also been observed and characterized at IBM Zürich [239] along with domain formation [240] and the thermal stability of these structures [241].  $C_{60}$  and  $C_{70}$  on Au(111) and other metal surfaces have also been observed [242, 243] with the consequent growth processes, domain formation and interfacial structures. Self-assembly of  $C_{60}$  on Au(110) has been examined [244] indicating that the underlying gold layer is modified by adsorption.

#### 3.7.4 Nonlinear Spectroscopy

Nonlinear spectroscopic techniques have been examined for a number of years to obtain information about materials. Nonlinear techniques associated with second-order nonlinearities adjacent to an interface are sensitive to the few monolayers of a fluid that have no center of symmetry, and correspond to one of the few methods to probe that very important interface. The technique referred to simply as "Second Harmonic Generation" (SHG) gives a frequency doubling due to this non-centrosymmetric region, but provides little in the way of diagnostic information such as spectral lines with which to identify the species responsible for the signal.

### 3.7.4.1 Second-Harmonic Microscopy

The second-harmonic microscope was discovered/developed at the Swiss Federal Institute of Technology; one of the researchers is continuing this seminal research in Münster [245, 246]. There are two other locations where this type of research is currently taking place: 1) Berlin, and 2) Mainz.

In this form of microscopy, an IR laser (Nd-YAG) is directed at a sample film (an in situ LB film, for example) from beneath the microscope. The non-centrosymmetric interface at the LB layer produces second harmonic photons. This beam is filtered to remove the fundamental 1.06  $\mu\text{m}$  radiation, and the 0.53 doubled light is focused in a microscope. This shows spatial images and variations several microns in dimension at the interface in which the field gradients have produced the anisotropic medium and the second harmonic. The SHG patterns produced by this method may be compared with those produced by cross-polarized filters [247]. There is a distinct resemblance between the images produced by the two methods, however there are some clear differences. This is really a method for measuring effects due to higher-order polarizability tensors, and gives additional information about structural details at an interface.

This new form of microscopy appears to offer advantages and new information from which a variety of behavior associated with domain formation and lateral fluctuation of thin layer properties, especially molecular layers, may be examined. One phenomenon currently being investigated by this method involves the growth of a domain by the application of electric fields in a LB film. This research is just now being initiated.

### 3.7.4.2 Sum-frequency Spectroscopy

Sum-frequency spectroscopy uses the same nonlinear coefficient as SHG but allows one of the frequency components to be swept, thus obtaining the nonlinear coefficient as a function wavelength. The spectra thus produced provide considerably more information about the thin film adjacent to the solid interface. Researchers at Oxford are introducing this technique as a method of examining that interface. With it, the identities of counter ions bound to a surfactant monolayer on a gold interface have been examined [248]. Stacking information for surfactant molecules have been examined [249, 250] providing information about the molecular orientations at a hydrophobic interface.

### 3.7.4.3 Chemical to Mechanical Energy Conversion

An interesting sidelight has resulted from an improved understanding of surfactant interfaces at Oxford. The result has demonstrated the conversion of concentration/surface tension effects to mechanical energy. By placing a small amount of a fluorinated fatty acid (amphiphilic molecule) in a droplet of water, and by placing the droplet at the end of a capillary tube, the fatty acid coats the tube, making the surface hydrophobic. However the aqueous solution continues to be attracted to the uncoated portion of the tube. As the meniscus of the liquid moves up the tube, the fatty acid continues to coat the tube on the "back" side where the droplet has been. The result is a droplet of aqueous solution that "walks" its way up the outside of the capillary, apparently defying gravity [251].

### 3.7.5 Surface Plasmon Microscopy

Yet another sensor technique is introduced with the concept of Surface Plasmon Microscopy (SPM). Surface plasmons considerably enhance the electric field at a metal surface from that of ordinary reflection. This effect is responsible for phenomena such as Surface-Enhanced Raman Spectroscopy (SERS). If the reflected light from a thin layer of gold on an optically flat surface is observed as a function of angle, a critical angle exists at which the reflected light has zero intensity. The different phase of the surface



plasmons interfere with the specularly reflected light to give complete interference at the proper angle. At this point, any perturbation to the surface represents a major change in the conditions for plasmon-specular interference, and can result in a large signal relative to a dark background. This technique may be useful for the detection of biological events, and is under investigation at Enschede for such possibilities. It was possible to detect one nm of organic material on the gold with this technique.

### 3.8 Millimeter Waves/THz Frequencies

Terahertz frequencies (millimeter wavelengths; 1 mm wavelength has a frequency of 0.3 THz) represent a neglected region of the electromagnetic spectrum, probably due to the poor atmospheric transmission at these frequencies. In order to fabricate devices that operate at these frequencies, specific mm-wave lasers may be constructed. Alternatively, devices with nanometer dimensions have lower capacitance and operate inherently at higher frequencies. Applications envisioned that drive some interest in this spectral region include collision avoidance devices for automobiles and artificial sight for the blind. There are a number of scientific questions associated with these frequencies, and experimental techniques are becoming available for investigating the details in this spectral region.

#### 3.8.1 *Far IR Spectroscopy and Device Fabrication*

With the ability to fabricate nanoscale devices comes a renewed interest in studying electromagnetic behavior at terahertz frequencies. It should be possible to fabricate waveguides, antennas, and the complete analogous set of components to deal with radiation at these high frequencies (long wavelengths, if the infrared perspective is taken).

There are several strong laser lines obtained from methanol when pumped with a carbon dioxide laser. One of these at 118  $\mu\text{m}$  (about 3 THz) is readily available with cw power levels of 100 mW and serves as a basis for some initial experiments at Delft. A pyroelectric sensor serves to monitor the radiation. Polyethylene serves as a lens to focus radiation at this frequency. Material properties involving "quantum dot atoms," single electron structures, and a wide range of spectroscopic characterizations are envisioned as this laboratory develops. With these tools becoming available, it is envisioned that single quantum dot behavior may be examined, as opposed to arrays of quantum dots studied in other laboratories. Thus observations of ensemble averages will become precise observations involving the behavior of a single species. The increased sensitivity of these techniques should make such studies possible.

### 3.9 Charge Density Waves

Charge density waves have been observed in bulk materials such as "blue bronze," a potassium molybdate material, as well as in a number of other materials. These waves are due to an interaction of charge densities (pairing of electrons and holes) with phonon structures in a crystal. These "waves" are observed by measurements such as neutron diffraction, spectroscopy, and transport properties at temperatures generally less than 180 K, but in some cases up to room temperature. These phenomena have a critical temperature associated with them, similar to that with superconductivity. Because they occur in dielectric materials that are not conductors, they have not received a great deal of interest. There is now some thought at Delft of attempting to find such charge density waves in properly prepared two-dimensional structures. Although these effects have been observed in bulk material, the effect is a one-dimensional phenomenon (it occurs along one-dimensional chains in the medium). The effect may be compared with Pierels distortion, where the interaction between electronic energy levels and phonons takes place to correlate the charge distribution with the interacting vibrational structure.

### 3.10 Molecular Behavior

#### 3.10.1 Molecular Switching

A molecular structure, or electronic state, may be modified by the introduction of energy (light, electric fields, pressure, acidity, etc.) and converted to a second species. If this second species may be reversibly converted back to the original molecular structure through an additional impetus, this is referred to as "molecular switching." This will result in a change of color (photochromic behavior), or charge separation (piezoelectric effect), center of symmetry (chiral property, that rotates polarized light), or conductivity (transport) that may be observed on a macroscopic scale. These phenomena are envisioned for the storage of information and for other opportunities involving logic (although logical operations are far from being recognized in the current state of the art).

##### 3.10.1.1 Molecular Switching at the University of Groningen

A useful molecular configuration with considerable flexibility of design for molecular switching has been examined with a number of variations. This structure has the appearance of two units of three fused benzene rings (anthracene units), bonded with a conjugated bond at the center apex of each unit (position 10 of one ring, position 5 of the other; the resulting structure has the appearance of the letter "H" on it's side). Heteratoms such as sulfur and oxygen may be introduced in various positions to give variability and modify the energy levels.

Most important is the introduction of an additional single fused benzene ring at the edge of one of the arms of the "H" such that it interferes with the anthracene unit on the other side of the bridging double bond. Steric hindrance twists the otherwise planar molecule, resulting in a molecular species that has two optically active forms. This molecule now has chiral activity (optically active) and each optically active form may be distinguished by the different spectral absorption characteristics of right or left-handed polarized light. Further, the rotation constants of this type of molecule are more than an order of magnitude larger than most optically active materials, making it easy to distinguish small changes in optical activity or the population of one species over the other.

Further molecular engineering has been demonstrated by introducing two different groups (demonstrated with an amino group and a nitro group) on positions 1 and 9 of the anthracene fused ring system (the carbon atoms on one anthracene unit facing the one having the extra fused benzene ring). This makes the otherwise equivalent positions on the anthracene group inequivalent. Further, the charge-transfer nature of the extra fused ring to the two inequivalent groups makes each configuration have a very different optical-rotatory spectrum. The resulting material is reversibly photochromic, changing from a cis/trans ratio of 70:30 when irradiated with 365 nm light to 10:90 when irradiated with 435 nm light. A review of this and other molecular switching phenomena (organic materials for reversible optical data storage) is given in *Tetrahedron* **49**, pp 8267-8310 (1993).

##### 3.10.1.2 Molecular Switching with Calixarenes

The group of materials known as "calixarenes" have demonstrated considerable flexibility for specific interactions. These molecules have a large cage consisting of four bridged benzene rings with substituent groups attached to each benzene ring. The overall structure looks like a bowl with arms reaching out from the edge of the bowl. The cage has been made large enough for dimethyl formamide to become trapped in the cage.

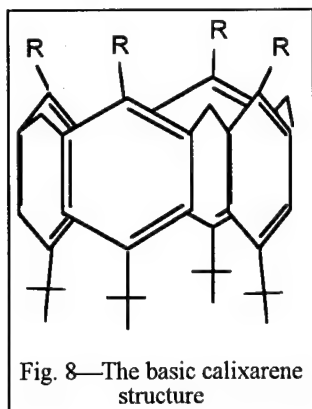


Fig. 8—The basic calixarene structure

A novel approach to making molecules that may switch between two stable forms is under way at the University of Twente. By starting with the calixarene structure [252] (see Fig. 8) and modifying the "arms" with another (inverted) "bowl" structure, an enclosed space (or cage) may be synthesized that is blocked at each end (two bowl-shaped structures, one at each end). If the two ends are made of different molecular structures, the resulting molecule has a dipole moment. Introduction of a molecule in the center of this cage gives a structure that can have multiple orientations of the internal molecule relative to the stationary cage. If the internal molecule has a dipole moment relative to that on the outside, two configurations (among others) will be with dipoles 1) aligned or 2) opposed. It is anticipated that one or the other configuration will be induced by an externally applied electric field, hence the concept of a

"ferroelectric molecule." Such an entity should demonstrate ferroelectric behavior without the need for cooperative phenomena, and can be "switched" by devices as simple as a scanning tunneling probe. Ideas such as this are driving the synthesis of some fascinating molecular structures at this university.

### 3.10.1.3 Molecular Switching with Intra-Molecular Electronics

The search for improved molecular switches is a major focus for efforts in the molecular electronics program [253] in France. The approach used in the program at Toulouse involves intravalent charge transfer, where two ions that may exist in two different charged states are linked chemically by a variety of molecular chains and/or linkages. Such a molecular arrangement gives rise to charge transfer bands, a phenomenon that has been studied in the chemical community for 30 years. By studying the charge transfer spectra of the complexes produced, insight may be gained into the strength of the interactions between the two oxidizable/reducible groups. The oxidation/reduction may be accomplished either by application of an electric current (voltage) or by photon excitation. Of course, the transport of a charge along the linking molecular framework is also of interest in these molecular complexes. Material properties that may be of interest for these complexes include non-linear optical properties, superconducting properties of a crystalline material, magnetic properties of molecular systems, high conductivity of non-metallic materials, and piezoelectric properties.

This overall approach has been termed "intra-molecular electronics [254]." Clever molecular design has provided additional data about a number of new complexes. The basic unit studied most often here, and which may be oxidized or reduced, is the ruthenium ion. This ion exists in the +2 and +3 state. Two of these ions are linked together by a variety of chelating systems, including various pyridines (one or two nitrogen atoms, each displacing a C-H group in a benzene ring), cyanobenzenes (one -CN group replacing a hydrogen atom on a benzene ring) and arrangements of these molecular groups linked together in a variety of structures [255-258]. Under certain circumstances the angle between two ring structures will twist in an excited state, reducing the interaction between the two ruthenium ions of an excited complex, and increasing the lifetime of the excited state [259]. Other "mixed-valence systems involving organic molecules have been studied [260].

Considerable data is being gathered in characterizing these structures. The philosophy driving this research program is one in which the future information storage devices may possibly use molecular switching as a means of storing information.

### 3.10.2 *Amphiphilic Materials and Oil Emulsification*

Very effective simulation capabilities for predicting the behavior of oil and water nanostructures in the presence of surfactants have been developed at Shell Laboratories, Amsterdam. Amphiphilic molecules are attracted to water with polar head groups on one end and hydrocarbons (oil-like) on the other. These molecules include the general class of surfactants, which allow water and oil to mix through the formation of emulsified clusters involving the surfactant with both ingredients. The manner in which these amphiphilic molecules provide the stimulus for emulsification has been simulated, with some interesting prediction of nanostructures through self-assembly as well as predictions of macroscopic behavior of commercial importance.

Simulation of the full lipid structure is very complex if all atomic interactions are taken into account. A simplified model was assumed here in which two "blocks" were used to construct these amphiphilic molecules: 1) a block that was attracted to water, and 2) a block attracted to oil. A Leonard-Jones potential was assumed for the oil-oil and water-water interactions, but only the repulsive potential function was assumed for the oil-water interaction. The degree of prediction available from this simple model is impressive [261-272].

Molecules consisting of various numbers of blocks were modelled in molecular dynamic calculations using cluster sizes of some 30,000 molecules (of which, for example, only 2,000 were surfactant molecules). The formation of a bilayer through the attraction of the "hydrophobic hydrocarbon tails" was clear with such a cluster of molecules involving a "surfactant" with one hydrophilic head group. However, if the number of hydrophilic head groups was increased to several "blocks," different shaped clusters appeared. In some cases the geometry of the shapes of this surfactant material became elongated (cigar shaped). With experimental verification of this behavior, a new method for designing and varying the viscosity of solutions was discovered.

Further, it was predicted that tubular or cylinder structures of these surfactant clusters should be particularly effective in emulsification processes. Again, experimental verification was obtained of this behavior, leading to approximately a factor of ten increase in the emulsification rates with the use of such surfactant materials. This process is now being tested for potential use by the company.

### 3.10.3 *Conductivity of a Single Polymer Molecule*

The lure of measuring the conductivity of a single molecule is attracting attention at the Technical University in Delft. A project is being initiated in which an eight-year effort devoted to this measurement is underway. The current effort is looking at polymer molecules deposited on a flat surface that contains a 10 nm gap between gold or platinum leads. The surface is examined with a scanning probe to determine the characteristics of the molecules dispersed on the surface (by spin coating, right now).

In addition to the effort in Delft, several other universities have programs to investigate this question. The behavior of electron transport through a molecule is a question of considerable importance, but one in which few measurements have been made. It represents a scientific challenge with unseen consequences.

### 3.10.4 *A "Crystallization Chip"*

Discussions at the University of Groningen revealed the idea a "crystallization chip" that has been pursued for years. This is a material with charges or structure arranged in a specific ordered manner in order to induce crystallization in a hard-to-crystallize biological sample. It is hypothesized that if nanostructures could be fabricated with just the right repetition distance (typically 5 to 30 nm apart) to

match that of a biological molecular crystal, then contact with a solution of the biological material could induce crystallization. There is considerable difficulty in getting some proteins to crystallize today. Further, some biological species may show two-dimensional order if exposed to such a regular template that matched the molecular dimensions.

This idea is a possible application of nanoscience for the benefit of medicine and additional scientific pursuits using the benefits of crystal structures and hence molecular structure that may be obtained from single crystals only.

### 3.11 Mechanical Behavior

#### 3.11.1 Surface Roughness and "Nanosurf"

Several instruments built for measuring surface roughness are impressive in their careful design, precision, and reproducibility at the National Physical Laboratory (NPL), Teddington. To measure surface roughness, a precision set of rails made of zerodur (a low coefficient of expansion glass) is fabricated and used to support a moving table that supports the sample on which the measurements are made. Instruments for performing this type of measurement are termed "Nanosurf MOD#." Early designs for measuring surface roughness (NANOSURF II) had a diamond stylus resting on the sample as it was moved under the probe. Nanosurf III uses interferometric detection of motion of the diamond stylus, and has a limit of 12  $\mu\text{m}$  of dynamic range vertically with 1 nm position sensitivity over a horizontal distance of 100 mm. Nanosurf III has interferometric capabilities only in one dimension.

Nanosurf IV is capable of motion in two dimensions (the x-y plane) and can examine a 100 mm  $\times$  100 mm sample. This instrument is capable of characterizing a sample surface topography to within 1 nm over this sample size.

Using a slope-integration method of observing a deflected laser beam (which gives the surface slope) and integrating this slope over the length of a scan, uncertainties of 4 nm are obtained over a 300 nm distance. The slope must be measured to an accuracy of 0.001 arc second for this level of precision.

With these precision instruments it turns out the largest sources of uncertainty are the thermal gradients over the sample and instrument. A thermal gradient of 0.05° C can make a 4 to 5 nm difference over a distance of 160 mm.

#### 3.11.2 Surface and Interface Roughness with Diffraction

Surface roughness is a property that can be measured by various means at NPL. Local probes such as STM and AFM are able to measure surface topography with such detail as to give considerably improved information on a nano-dimensional scale. Comparisons between STM measurements and X-ray diffraction patterns, formerly used to measure fluctuations and hence crystallite size, show some interesting differences. Likewise, differences between intentionally prepared layered structures measured at low angle X-ray scattering and those at high angles show differences and marked discrepancies. The basis for the different crystallite sizes and layer uniformity measured by these methods is understood based on different correlation lengths measured inherently by the two different techniques. Each technique is obtaining an average over a different dimension of a sample, which is the cause for the apparent discrepancy. An alternative approach to making these measurements is suggested in order to avoid errors to which each technique is susceptible [273].

### 3.12 Standardization with Nanostructures

#### 3.12.1 Accuracy and Precision of Measurements with STM/AFM

Measurement of the width of a 0.2  $\mu\text{m}$  line on a surface may be accomplished today with about 10 percent accuracy. There is a clear need to understand how instrumentation limits the fidelity of features being observed with surface-measurement tools. A general approach to such limits of measurement was introduced several years ago at the National Physical Laboratory, Teddington [274-276] and is being applied to STM/AFM instrumentation [277-279]. Clearly the radius of curvature of a stylus instrument limits the lateral resolution associated with any such measurement related to "wave length" in the lateral direction. Similarly, measurements in the vertical direction are limited by a dynamic range and a vertical resolution limit due to the sensitivity along that direction. Likewise a given surface may be characterized by a distribution of lateral feature sizes and amplitude ranges. By plotting the characteristics of the measurement instrument and of the sample under study in a two-dimensional plot of amplitude and wavelength, the limits of measurement for that sample for that instrument become clear.

Certainly the characteristics of commercially available instrumentation are of interest to any buyer, and the manner in which these limits are stated amount to a standardization of the language used to convey this information. This is the ultimate goal of these standardization efforts associated with limits of measurement.

#### 3.12.2 Standardization of Nanonewton Forces

A force exerted by an atomic force microscope is on the order of  $10^{-8}$  N (or one microgram). The standard kilogram is known with an accuracy to one part in  $10^9$ , which corresponds to one microgram. Force constants of AFM instruments change with time, linearity is a problem, and electromagnetic and electrostatic forces must be properly considered. If standard pressures are desired, for indenters for example, the additional challenge of measuring lateral dimensions is introduced. Improvements in the precision (and accuracy) of such measurements is being addressed at the NPL.

A probe (such as a local probe) may be positioned interferometrically to within 0.5 nm (one standard deviation) [280]. Some degree of linearity is possible with interferometric measurements. Problems of stray reflections, polarization differences, etc. must be addressed to reduce the uncertainty of these measurements. These many practical problems will affect many scientific and industrial efforts in the future.

### 3.13 Instrumental Developments

Although a number of instrumental developments appeared throughout the many laboratories visited, most of these were associated with specific directions for fabrication, measurement, or utilization. The following instrumental developments are sufficiently general that they are not readily classified by such criteria.

#### 3.13.1 Inertial Stepping Motor for Nanometer Instrumentation

A small motor has been designed, built, and used for precision positioning (within one arc second) of the rotation of a sphere about arbitrary angles [281]. Rates of rotation are on the order of degrees per second. A metallic sphere is held magnetically against three piezoelectric arms. The arms move slowly to advance the sphere in the direction desired, then return to their original position rapidly. Frictional forces advance the sphere during the slow step, whereas the inertia of the sphere prevents it from following the



arms back to their original positions. Mechanical backlash is eliminated with such a design. The advantages of this instrument are illustrated in its use with a multifunctional local probe instrument for remote adjustments of optical beams (see subsequent paragraph).

### 3.13.2 Multifunctional Local Probe

A local probe instrument has been designed and built for measuring lateral forces, normal forces, and tunneling currents simultaneously in an ultra-high vacuum [282-285]. Deflections of LED light beams to the cantilever are controlled with the inertial stepping motor described in the previous section. These beams then fall on a quadrant detector to sense motion. The LED has certain stability advantages relative to a laser diode for such applications. Atomic resolution in the STM mode is readily obtained with silicon and sodium fluoride samples. In the SFM mode, features separated by 3.2 Å are recognized. Additional instrumentation has been introduced to improve mechanical and thermal stability on standard AFM instrumentation [286].

## 4. POTENTIAL UTILIZATION

A number of uses involving nanostructures have been mentioned in the previous sections associated with fabrication and characterization. Programs that have applications as a focus are described in this section of the report.

### 4.1 Devices in Electronics

A major driving force for the fabrication of miniaturized electronic devices is the digital and high frequency communities. Although a major economic impact is clearly seen from chips fabricated by lithographic methods, a number of niche utility devices are becoming apparent for nanodevices. Attractive properties for certain devices may well establish niche markets. Some of these are mentioned below.

#### 4.1.1 In-Plane Gate Transistors (IPGTs)

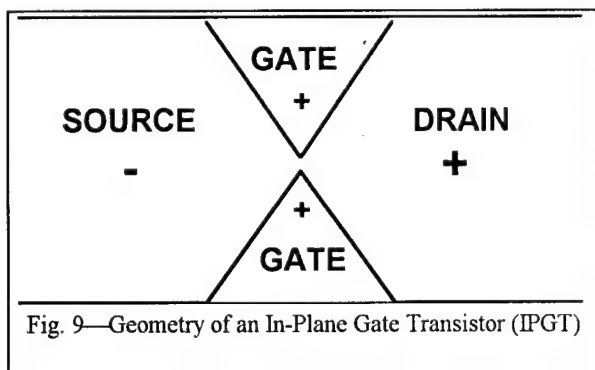
The in-plane gate transistor should not be confused with transistors in which the action of the gate is induced by field-effects of an electrode above a conduction channel (such as an HEMT). Rather, the "in-plane gate" is a device originating at the Max Planck Institute in Stuttgart, Germany, by Andreas Wieck. The device is formed in a heterojunction conduction channel by fabricating an insulated area around the gate, with conduction through the channel controlled by induced depletion effects as a voltage is applied to the gate (see Fig. 9). This gate is formed either by ion implantation or other means such as ion diffusion.

Dr. Andreas Wieck is in the process of moving from the Max Planck Institute in Stuttgart to Ruhr-University Bochum in Bochum, Germany, where he is setting up a group to expand the research that he has initiated.

##### 4.1.1.1 IPGTs by Ion Beam Implantation

Focused ion beams (FIBs) have been used to produce the first in-plane-gated transistors [287-292]. This was accomplished by depositing gallium onto a 2-DEG to create thin insulating lines. The gallium produces, in effect, two opposing n-p-n transistors across the deposited line. By leaving a small portion of this barrier open, a channel for conduction may be formed. By arranging two "v-shaped" figures nearly touching each other in the middle of a 2-DEG, the transport between the two triangular apex regions is constricted and may be influenced by voltages applied to the triangular portions through lateral depletion effects. This is illustrated in Fig. 9.

These designs have been used by other researchers, and represent a way to fabricate transistors with single implantation operations using a FIB. One advantage such devices have is a small capacitance, about



1/10th that of other types of transistors (approximately 0.3 femtofarads/micron). Bipolar transistor behavior may be introduced by using n-p-n materials. More complicated patterns may be introduced by interacting devices. It is interesting that the circuit design is represented with lines and areas, similar to the usual circuit design in electronics, but with these devices the areas represent the material behavior and the lines represent the insulated areas (just the reverse of the usual notation in circuit design).

Design variations may be introduced to vary the transistor characteristics. An example was shown in which the slope of the I-V curve was varied, and made symmetric or asymmetric, simply by changing the degree of tilt of a gate line abutting against another line (different design). This, then, offers unipolar rectifiers! These devices should offer the opportunity to fabricate ring oscillator devices. At high frequencies the high impedance of these devices is a problem (the usual required match of impedances to a 50-ohm lead). The degree of flexibility offered by this approach seems to be considerable.

This fabrication approach offers considerable flexibility in circuit design. Further, in order to fabricate these devices one need only implant a line, not an area, with implantation numbers of approximately 100 ions per micron. Apparently Daimler-Benz in Ulm is working with these devices for design of future systems.

The instrumentation for ion beam implantation in Stuttgart includes 100 keV gallium beams that can deposit patterns with approximately 100 nm resolution. A new column is almost finished (and will be transferred to Bochum, Germany) that will deposit  $\text{Ga}^+$  30 nm beams at 3 pA current. This beam will deposit 16,000 bits per 0.5 mm, and can work with four 3-inch wafers. This machine will be able to separate the isotopes of  $^{69}\text{Ga}$  from  $^{71}\text{Ga}$  by magnetic field deflection. Also, a beam of gold/silicon/beryllium may be focused to 30 to 100 nm resolution with a few pA current at 100 keV. Magnetic deflection enables the use of any of these atomic beams for deposition. These ion beam instruments are purchased from Japan.

#### **4.1.1.2 IPGTs by Diffusion to Give Enhanced Resolution**

Various nonlinear means of obtaining nanostructural resolution substantially less than the diffraction limit of light have been used. One such method introduced at the Walter Schottky Institute in Garching, Germany is the diffusion of a species placed on the surface of a semiconductor. An example is that of zinc, which is a p-type material in GaAs. A coating of zinc, when heated with a stable (1 part in  $10^4$ ) Argon ion laser beam induces zinc to diffuse into the n-type GaAs substrate nonlinearly, producing an 0.1  $\mu\text{m}$  quantum wire (a factor of five smaller than the width of the Argon ion laser beam).

Using this as a fabrication tool, it is possible to make an in-plane gate transistor [293]. The p-type nature of zinc in n-GaAs acts as a barrier (in effect, two opposing p-n junctions). This novel method of fabricating such a transistor has attractive features for design and simplicity.

A similar technique for using diffusion effects to produce smaller than diffraction-limited lines has been used (in collaboration with researchers in Ulm) to produce 80 nm wires using a holographic grid from a 320 nm uv cw He-Cd laser.

### **4.1.2 Memory Devices**

#### **4.1.2.1 Thermally Erasable Memory with STM**

Some scanning probe microscopy at the Technische University of Munich, Germany involves modification of a passivated amorphous silicon surface that has been doped with phosphorous. A minimum exposure of this surface to electrons from a scanning tunneling microscope tip modifies the phosphorous from  $\text{P}_3$  to  $\text{P}_4^+$ , which is an insulator. A larger exposure makes a better conductor with an increased density of defects in the material.

This scheme could be used as a possible memory device by recording bits of information through pulses at the tip. The recorded information may be removed by heating, which anneals the damage. This is a possibility for a thermally erasable read-multiple memory.

#### 4.1.2.2 Photon Imaging of Gold

Photon emission from certain metallic surface excited with the electrons from an STM has been observed for several years. This photon emission is a result of plasmon excitation of the gold particles, and is clearly observed with the appropriately prepared rough surfaces of gold and silver. A group at Toulouse, France has observed interesting structures in gold, where the image produced by photon emission is markedly different than that obtained for topography. The photon emission from gold may be highly dependent on the orientation of the crystal lattice, or the direction of the emission may be directionally dependent; the explanation of why some crystallites emit much more readily than others is not yet clear.

The metal-semiconductor interface may be studied by Ballistic Electron Emission Microscopy (BEEM) in which the electrons emitted from a tunneling tip traverse several hundreds of angstroms through the gold metal (a relatively long mean free path) [294, 295]. Scattering from a submerged gold-semiconductor interface produces a signal which may be imaged to obtain information at the interface several nanometers beneath the gold surface. It is interesting to compare topographic images with BEEM images. The lateral resolution of this technique is on the order of several nanometers (lateral resolution approaching the vertical separation).

While studying this process it was noted that the plasma excitation and resultant photon emission from gold on mica could be modified by application of appropriate voltages, and the image could be written with clearly observable patterns [296, 297]. This is done in air with few special precautions. The surprising observation was also made that this process could be made reversible by reversing the voltage. This forms the basis of a patent that the laboratory has on this phenomenon, since reading and writing reversibly with a tunneling tip could be the basis for information storage and retrieval.

#### 4.1.3 Terahertz Devices and Systems

##### 4.1.3.1 Integration of THz Components and Devices

For a number of years various efforts experimenting with millimeter wave devices (or THz frequencies) have been supported in fragmentary ways. An effort at Nottingham is now attempting to integrate the various advances that have appeared in 100 GHz to 1 THz devices demonstrating advantageous performance features. This ambitious project is just beginning, and a variety of oscillator, transmission and detection devices are being assembled. Some initial systems that are being considered for practical application include 1) mobility aids for blind people, and 2) short range telecommunication devices.

When the components are viewed for these devices and systems it becomes obvious why this is a challenge. A waveguide for 600 GHz radiation is fabricated by ablating a hole in a resist with a laser and coating metal over the structure, which has a cross-section of  $20\text{ }\mu\text{m} \times 100\text{ }\mu\text{m}$ . There is some feeling that 450 GHz may be a practical upper limit with GaAs devices, but 700 GHz is projected with InSb devices. When viewing the integration problem, it becomes obvious that there is a great need for active devices for use with wave guides, etc. in the far IR.

There is some indication that THz frequencies cause substantial effects on biological systems. This is an area that can be investigated once integrated devices are available to the experimentalist.

#### 4.1.4 Whiskers As Terahertz Mixing Devices

The venerable cat-whisker remains as the choice structure for mixing high frequencies. The reason for this is that such a structure, where a metal whisker is in contact with an appropriate metal through a bit of oxide (a Schottky barrier), the low capacitance of this geometry is as small as any device made that will give the asymmetric I-V relationship necessary for high frequency mixing. With whisker diameters of 0.5  $\mu\text{m}$ , capacitances of 0.1 femto-farads are obtained. These devices are used today for mixing of frequencies up to 2.5 THz. These whisker mixers are made at the Technische Hochschule Darmstadt, in Germany, by placing Au whiskers in contact with Pt/Au junctions over GaAs for the Schottky barrier. The noise performance is critically dependent on the interface properties of the various junctions made. The Au tip radius is 0.5  $\mu\text{m}$ , and the Au whisker diameter is approximately 15  $\mu\text{m}$ .

These whisker mixers are produced in only a few fabrication facilities in the world, and are supplied to radio astronomy laboratories and environmental satellite probes throughout the world.

Some concern is expressed about the requirement to provide space-qualified junctions that will withstand the rigors of satellite launch and the stresses in outer space. Modified Schottky contacts are being prepared so that the whisker is in contact with the Pt/Au in a more stable spring-loaded geometry for such requirements.

#### 4.1.5 Electron Beam Instruments

The design of electron beam instrumentation has taken a decidedly new twist. From 100 keV machines that stood ceiling to floor, and from multiple correction fields necessary to remove aberrations limiting high resolution electron beams, the design frontier now shifts to micron scales with interesting results.

An electron beam from an emission tip generally spreads out several degrees due to the limitations in geometry at a typical tip. There is active theoretical work under way at FTZ, Darmstadt to shape emission tips. If the field at an emission tip has the proper gradients, a focusing of the emitted electron beam may be obtained. This should result in a significantly narrowed beam useful for both instrument development as well as improved lithographic definition by such beams.

Further, years of experience have demonstrated how to improve the focusing of an electron beam [298, 299]. At FTZ, Darmstadt, it is possible to grow 0.1  $\mu\text{m}$  diameter metallic or semiconducting wires with high aspect ratios (20:1) in specifically chosen directions [300, 301]. This fabrication is accomplished by focusing an electron beam on a substrate while effusing a low-pressure organometallic precursor beam onto the surface. The molecules of the precursor diffuse on the surface to the position at which the electron beam is focused and are then decomposed (with the concurrent deposition of the metal). Since the electron beam may be focused tightly, the structures resulting from this approach are sub-micron and of high quality.

With the ability to design electron optic components at sub-micron dimensions, devices are anticipated at terahertz frequencies. Using 1933 principles, a miniaturized dynatron may be designed that takes only a few microns of space. This has been under investigation by Matsui in Japan (a part of NEC) since 1984. With these new instruments it is hoped that THz oscillators may be readily available in the future. In such a device, the field emission tip is made of two intersecting 0.1  $\mu\text{m}$  diameter metal wires. An electron beam passes through two triangles made from the same wire-fabrication technique described above. The resulting beam broadens spatially from 2 nm at the emission tip to 20 nm over a distance 10  $\mu\text{m}$  away (0.002 radian divergence). At these dimensions, the greatest effect limiting the focus of these beams is that of diffraction rather than any further refinements in the aberration limitations.

## 4.2 IR Detectors

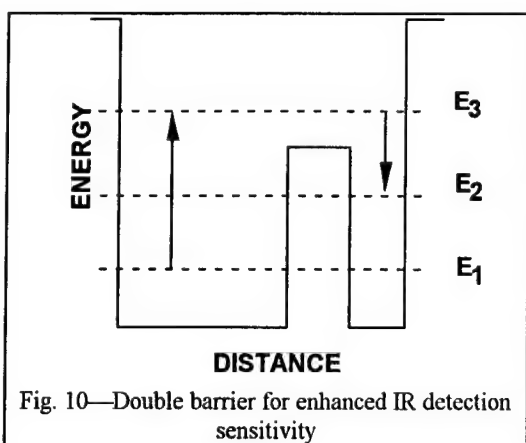
Improved detectors for IR radiation take the form of 1) old principles at micron or sub-micron dimensions, such as a thermocouple or a bimetallic strip, and 2) semiconductor heterojunction materials designed with band gaps and geometries as to enhance the detection limits. Clever designs are being introduced to take advantage of the properties of materials having sub-micron dimensions.

### 4.2.1 A Fast Sensitive Thermocouple

Work at the Cavendish Laboratory in Cambridge, U.K. involves the fabrication of IR detectors using copper/constantan couples (like the old traditional thermocouples of years ago). The difference is the scale of the fabrication. Wires of copper and constantan are fabricated lithographically by deposition through suitable masks. The wires are approximately  $1\text{ }\mu\text{m}$  wide,  $0.1\text{ }\mu\text{m}$  thick, and  $20\text{ }\mu\text{m}$  long. The etching takes place such that the wires are freestanding, supported by larger plates resting on pedestals that have not been completely eroded by the etching process. These devices are broad-banded and have an impressive responsivity and response time at room temperature, a desirable characteristic for such detectors. They have a noise equivalent power of  $3.9 \times 10^{-9}$  watts/ $\sqrt{\text{Hz}}$  at  $10.6\text{ }\mu\text{m}$  wavelength with a  $20\text{ }\mu\text{s}$  response time. Their responsivity is enhanced by coupling a number of junctions in series (as many as 100 junctions have been coupled in experiments thus far).

### 4.2.2 Improved Heterojunction Materials for IR Sensors

The design of quantum wells to optimize the transition probabilities between energy levels has become a matter of considerable sophistication as well as speculation at Thompson CSF [302] in Orsay, France. It can be noted that the wave functions for the first two levels of the above illustration are located on decidedly different sides of the potential function. Thus any transition between them involves a very significant shift in the center of charge for the material, and this then becomes the basis for a photocapacitive detector. This type of detector has a useful functional dependence on angle of incidence, being rather level and independent of polarization for wide angles. A problem associated with it is the lifetime of the excited state, which limits the sensitivity. If longer lifetimes can be designed into the system it would perform better.



Thus a modified potential function has been introduced that is asymmetric and is illustrated in Fig. 10 [303].

Transitions from  $E_1$  to  $E_3$  relax to  $E_2$ , which have a significantly different center of charge than  $E_1$ , resulting in charge displacement that may be detected [304, 305]. By changing the width between the two quantum wells the lifetime of the  $E_2$  state may be modified. With such a device sensitivities of about 60 microvolts for an illumination intensity of  $6.3\text{ W/cm}^2$  have been found. Additional design improvements have included fabricating lateral gratings into the front face of these detector materials in order to scatter the incoming light laterally,

thus enhancing the absorption length of incoming photons. By clever design of these potential wells along with other design improvements, factors of 300 in sensitivity of these detectors have been gained over the last three years.



Additional ideas related to gaining yet further improvements in relaxation time by designing forbidden sub-band transitions through physical geometry constraints are being considered for future research directions [306]. Strained quantum well materials introduce yet another variation to be explored [307]. Designing photonic band gaps into materials such that emission at the natural wavelength is forbidden, represents yet another use of nanostructured materials that may improve such detectors substantially. Such ideas have been attempted in the past, but require an improved understanding of the factors associated with sub-band relaxation effects and transition probabilities.

#### 4.2.3 *Microwave Sensors*

Theoretical calculations indicate the quantum wire may be used as a microwave sensor (in effect, an electronic bolometer). An advantage of such a system is that the optimal frequency may be tuned by voltage, simply by changing the dimensions in a 2-DEG. Calculations suggest that such a device would be tunable from 2 to 12 THz. Laboratory experiments are working with 300 of these devices in parallel at the University of Munich in Germany.

### 4.3 **Optical Components**

The ability to fabricate structures approximating the wave length of light introduces some interesting effects involving diffraction and light modulation. In addition, confinement effects modify the energy levels of quantum dots and wires, leading to new spectroscopic properties with potential utility for active gain media with lasers as well as narrow specialized filters. These latter potential applications are discussed in the section under quantum dots and wires.

#### 4.3.1 *Optical Modulators*

##### 4.3.1.1 **Wannier-Stark Effects for High-Speed Optical Modulation**

Wannier-Stark ladders have been under study at l'Ecole Normale Supérieure, Paris and have been recently reviewed [308]. Heterojunction materials having a number of adjacent layers are represented in a zero electric field as having a band gap due to the interaction of the levels of each well. Semiconductor superlattice spacings for such materials are on the order of 50 to 100 Å.

In an electric field, the degeneracy of these bands is broken due to the shift in energy for each well relative to each neighbor. The degeneracy of the bands is broken, and a number of bands with gaps between each one may be obtained. This Wannier-Stark ladder forms the basis for a spectroscopic band edge that is very sensitive to electric fields [309-311]. This is analogous to the Franz-Keldysh effect in a bulk material. However, with this heterojunction material, the shift of the absorption band edge is much more sensitive to an applied electric field.

Using such materials, a 100  $\mu\text{m}$  long piece of material between two optical fibers has been used to modulate a light beam 20 dB with an applied voltage of only one volt at 20 GHz. Thus much lower powers are required to modulate light beams with this effect. These devices have caught the attention of researchers at CNET, the French telecommunications company, and apparently are being introduced for certain telecommunications functions. Frequency limits are solely determined by the RC time constant of the coupling device; higher frequencies than 20 GHz are possible, but at a reduction of the modulation level.

In some laboratories there has been speculation that transitions between the Wannier-Stark levels could be used to excite oscillations at frequencies corresponding to the energy level separation. This appears to

be quite difficult, since the absorption by the energy levels producing the oscillation are expected to be as strong as the emission, canceling any tendency to oscillate.

#### 4.3.2 *Continuous-Relief Microoptical Elements*

Binary optics has been a subject of study for a decade; in binary optics a geometric pattern of transparent and opaque materials form a pattern to diffract light. These patterns have the function of refracting light in much the same manner as lenses and other refracting media.

Continuous-relief microoptics is based on much the same principle, except rather than transparent and opaque materials, continuous relief of the surface is fabricated [312]. The efficiency of these devices is generally better than that from binary optics. A lens thus is represented as several concentric rings with slopes and curvatures representing the curved surface of a lens, but condensed onto a much flatter surface through several folds. Gratings and fan-out structures may also be fabricated with these techniques. For typical elements, the maximum relief depth is about 5  $\mu\text{m}$ . Initial fabrication of such a structure is accomplished by either diamond milling or writing on a photoresist with a focused laser beam (with subsequent controlled processing). Such structures may then be mass produced with processes such as hot embossing, molding, and casting [313].

#### 4.3.3 *Buried Grating Nanostructures*

An interesting optical property may be observed with buried metal or dielectric grating nanostructures at the Paul Scherrer Institute in Zürich. Closely spaced steps are fabricated and filled with a second transparent material having a different index of refraction. The steps must approach distances substantially less than half the wavelength of light (for visible effects, line widths of below 100 nm are used). These gratings have strong polarization dependence. When viewed in ordinary white light, this surface changes color with rotation of the sample in the plane of the sample. This effect cannot be duplicated with photographic equipment, thus it becomes an interesting alternative for fabricating secure documents (such as credit cards or money). Another possible use of this material is as a filter that transmits visible radiation but blocks infrared radiation, having possible utility for energy conservation. Surface relief replications have the potential of realizing nanostructures using low cost mass production techniques such as hot embossing or injection molding. It is possible to obtain one nm resolution by embossing techniques!

#### 4.3.4 *Other Grating Innovations*

By coupling semiconductor laser emission into a grating the beam may be directed perpendicular to the surface and focused at a point. This is likewise possible for coupling the reflected beam to a detector. This results in substantially less complexity than the arrangement used with current compact disk (CD) instrumentation, a project at Chalmers University, Göteborg.

#### 4.3.5 *Monolithic Interferometric Sensors*

The utility of the Mach Zender interferometer for sensing small changes in the index of refraction between two arms of the interferometer is well known. By fabricating grating structures to obtain efficient input and output of a laser light source, and by guiding the light to two arms of the Mach Zender interferometer, a sensitive measure of changes in the surface properties due to an adsorbed monolayer may be sensed. This structure is being fabricated for detecting the presence of biological antibody-antigen interactions at the Paul Scherrer Institute, Zürich. With the mass production of such devices, inexpensive sensing components may be placed on a light source and detector for sensitive detection of specific

biological materials. The inexpensive nature of the cell (pennies per interferometer/grating combination) makes this an attractive possibility for rapid screening of many samples.

## 4.4 Sensors

### 4.4.1 *Sensors for Monitoring Engine Performance*

The opportunity to monitor engine performance with a wide variety of new sensors emerging from the field of micro/nano technology is leading to a 12-year program supported by the Deutsche Forschung Gemeinschaft. The Technische Hochschule Darmstadt is a primary activity in this overall effort. The advantages of GaAs make it likely to be used for a number of purposes. First, if sensor performance can be obtained from GaAs, it is quite likely that any voltages obtained from the sensor may be readily integrated into electronic processing on the same chip. Silicon carbide is another semiconducting material on which this might possibly be accomplished, however the silicon carbide technology is not as mature as that of GaAs for use in integrated circuits. Any other material must still be integrated onto a chip for processing, so the best material overall for the high temperature measurements in a combustion engine appears to be GaAs.

GaAs may be used to sense pressure, as it is piezoelectric (silicon is not). In a combustion chamber of an internal combustion chamber, one would like to sense the pressure as a function of time (within a single stroke) in order to change the feed to the engine. The sensor that can do this is a MESFET with a GaAs strip that has an extension over the gate region of a source/drain transistor. Any strain on the GaAs will change the position of the extension over the gate region, resulting in a signal in the source-drain current. Pressures of 20 bars may be measured with this sensor (however 80 bars are needed for desired measurements, a current technological challenge). It is anticipated that such a sensor will be in a motor within two years.

Another interesting sensor is one that could measure tire contact with the road. It is desirable to detect when a tire is sliding on water or ice, for example, so preventative action may be taken to avoid a skid. Tire studs are constantly being flexed. In a skid, the amount of flexure changes substantially. Thus, magnetic sensors are being built into tires to measure the amount of displacement for each turn of the tire on a single rubber protrusion on the tire. By positioning a small magnet near a protrusion on a tire, and by locating a magnetic sensor close to the magnet, the motion of the magnet may be sensed to determine the motion of the rubber protrusion. A magnetic sensor that uses a split drain transistor appears to be the most desirable. In this sensor, current that is split into each of two drain regions of a transistor fluctuates with magnetic field and this appears as a voltage signal that can be balanced with a counter voltage applied to an appropriate gate on the device.

Flow sensors are taking the form of determining the flow of air through a small bridge. This bridge is built over a heat sink with a bridging GaAs/AlGaAs heterojunction (which has a small thermal conductivity). A heating resistor is placed on the center of the bridge, providing a steady state thermal profile for the heterojunction material. When a gas flows over this device, it is possible to measure the change in the heat conduction due to the passing gas with a voltage resulting from the changing resistance of the heterojunction material. Such a device could also distinguish between different gases (they have different thermal conduction coefficients), and pressures of 1 to 1000 Pascals can be measured. With differential measurements from two orthogonal devices, it is possible to measure the direction of air flow. This could be used to detect stalls in turbines to allow automatic corrective action.

These devices could also be used as infrared detectors by adding black platinum to absorb IR radiation. The Seebeck coefficient for n-AlGaAs/p-AlGaAs junction is approximately one mV/K, whereas that of

copper/constantan is approximately 40  $\mu\text{V/K}$ . Thus, the AlGaAs material is a more sensitive sensor for temperature changes.

Due to the piezoresistance of GaAs, this material is also able to detect membrane distortion. Such a membrane could be used as a pressure sensor or even as a microphone.

#### 4.4.2 Chemical/Bio Sensor Phenomena

Sensors under investigation in the Chemistry Department at the University of Tübingen, Germany are based on a wide variety of physical principles. Experience with the molecular recognition principles is leading to the ability to design molecular structure to be specific to desired interactions. A number of the types of phenomena under examination at Tübingen are described.

*Changes in Mass:* The quartz balance is a quartz oscillator coated with selective coatings onto which adsorbed gases change the mass, changing the resonant frequency. This is a well-recognized method of sensing the presence of adsorbed gaseous species. It is less sensitive than surface acoustic wave (SAW) devices, but has the advantage that it does not require temperature compensation, thus leading to simplified circuitry. For many applications, the quartz balance provides sufficient sensitivity and the convenience is desirable.

The calixarenes are organic "semi-cage" compounds that may be "tuned" by changing the length of the chemical chain on a portion of the molecule. By this method, the size of the "pocket" in which molecular species interact is changed, allowing a molecular adjustment to species of a specific geometry and size. This is a method to design selectivity to desired molecular properties based on the size of the molecule [314-316].

*Changes in Transport Properties:* Semiconductor sensors are generally more sensitive than the quartz balance. By matching the energy level band structure with that of adsorbed molecules, specificity of changing transport properties adds an additional degree of information for identification of specific species [317]. Noble-metal doped tin dioxide, for example, is sensitive to carbon monoxide.

*Heats of Reaction:* Temperature changes, detected with an array of miniature thermocouples on which various materials have been deposited, provide for a thermal profile characteristic of specific gas-substrate interactions. An array of 64 thermocouples in a star configuration has been used for this purpose.

*Work Functions:* The voltage at which a surface emits current through an adsorbed coating changes with chemical composition. This adds another degree of freedom for selectivity and gas identification.

*Capacitance:* The capacitance between interdigitated electrodes changes as the dielectric constant is varied in the material between the electrodes. This may reveal resonant properties or a change in sample density or composition.

*Electrochemical Potential Differences:* Miniature electrodes placed in strategic locations with solid state conducting materials act as transducers for certain species present.

*Optical Absorption and Reflection:* Spectroscopy in miniature represents a trend to obtain spectroscopic information with clever design and miniaturization.

#### 4.4.3 *The Electronic Nose*

With the wealth of data available from the multiple sensor suite in such a laboratory, it is possible to envision a great range of information specific to each of many different gases. The uniqueness of a specific pattern for a given gas would allow identification of the gas. For gas mixtures, pattern recognition techniques serve to unravel the variety of interrelationships and identify the constituents.

A book has been written on this subject specifically for detailed sensor identification [318]; commercial electronic noses are appearing on the market today. Neotronics, in England, manufactures an Electronic Nose that sells for approximately \$20,000, complete with microcomputer for control, neural network software, and data reduction capabilities. This device uses a sequence of 12 conducting polymers in  $10\ \mu\text{m} \times 1\ \text{mm}$  active areas for each polymer. Sensitivities of this device are on the order of ppm for a large number of gases. Using a multilevel perceptron with one to two hidden levels and a backpropagation algorithm, this "nose" can distinguish wine from champagne, can tell fresh potato chips from stale ones, and can distinguish the smell of different kinds of paper. A second generation system will probably be offered soon that will provide more complex signal processing, reduce interference of humidity, and offer improved material diagnostics.

There is apparently considerable European interest in chemical sensors using techniques such as those employed in the electronic nose [319].

#### 4.4.4 *Selective Membrane Transport*

Considerable work has been done and is continuing at the University of Twente, Enschede, The Netherlands with the design and characterization of molecular receptors that are designed to pass specific ions and/or neutral molecules. This is done by designing cage compounds with specific sizes and attractive groups to bind selectively with targeted ions, and then this material is admixed with a membrane material. The combination of this selective material in a membrane (typically polysiloxane material) makes the membrane selective for the passage of the designed material. This area of "supramolecular chemistry" is concerned with the large molecular groups designed for specific functions. Incorporating these selective membranes on the gate of a field effect transistor (FET) makes the transistor selective to the chosen chemical material. This is termed an Ion-Selective FET (ISFET), which has been in production for a decade or more. However, selectivity for specific purposes is a continuing endeavor. Introducing such FETs on chips containing logical elements should give specific, intelligent, inexpensive, and sensitive (ppm) sensors for environmental, medical, and processing applications.

Examples that show selectivity to specific ions such as sodium, potassium, cadmium, silver, and/or copper were shown. A new and difficult ion for selective transport is the phosphate ion, for which a selective group has been successfully designed and synthesized. It was also shown that combining ion selectivity for both anion and cation introduces a high degree of selectivity for transport through a membrane for the single molecular species corresponding to the matched anion and cation. The specific species that has been designed through many laborious synthesis techniques is that of sodium dihydrogen phosphate (a problem environmental material due to contamination from fertilizers). With the molecular designs introduced, a selectivity ratio of better than 100:1 for this species relative to other species commonly present has been observed. Considerable innovation in molecular design of large groups with specially designed cage configurations is shown in the materials developed in this laboratory. Clearly, the ability to design nanostructures with specific functions is becoming a reality through such synthesis research.

A general principle for selective monolayer design was demonstrated by one student thesis whose objective was to prepare a large calixarene cage with  $140\text{\AA}^2$  area (external) attached to thiol groups that would bind to a gold surface. Many initial experiments failed for lack of obtaining a good monolayer. This research was finally successful when additional hydrocarbon chains were introduced such that the groups extending from the calixarene to the thiol linkage had the same area as that of the calixarene cage. The general principle was thus illustrated: to obtain good monolayer definition with long-chain molecules, the group attached to the surface must have a similar area as the group extended away from the surface. This material was made and demonstrated to have a high selectivity for the tetrachloroethylene molecule, which is used often in dry cleaning and other industrial operations and, thus, should be monitored constantly for environmental safety reasons.

In addition to sensing methods such as membrane transport, alternatives for measuring molecular interactions are being explored. One of these is the quartz microbalance, which senses a change of frequency due to molecular species that are absorbed into a layer of material selective to a given species. Specific materials for selected species are also made at the University of Tübingen in Germany. It is clear that cooperative efforts in these fields subtend national boundaries.

An ultimate goal of such research would be to make an array of such sensors with pattern recognition for multisensor selectivity and identification of environmentally and industrially important materials.

#### 4.4.5 *Surface Acoustic Waves and Chemical Sensing*

The use of the quartz microbalance for sensing small changes in mass such as represented by adsorption of a molecular monolayer has been recognized for a number of years. The SAW device has also been used for this purpose, and is inherently more sensitive for this function, as the mass involved with the oscillations is much less, and the higher frequencies give higher sensitivity in addition (the sensitivity is linearly dependent on frequency). At a liquid interface, however, the ordinary Rayleigh wave mode of propagation (compare with an ocean surface wave) generates waves in the liquid that propagate away from the SAW device, leading to a loss of energy and considerable decrease in energy.

Alternative wave propagation modes have been examined to determine if greater sensitivity may be possible in a liquid [320]. Among these, the Love wave is promising and is under study at the Paul Drude Institute in Berlin. This wave propagates as a transverse shear wave that becomes a surface wave if a second layer of solid material having a slower propagation speed is added to the surface. The transverse motion of this wave does not propagate energy into the adjacent liquid layer. However the optimum thickness of the second solid layer must be determined to obtain the maximum sensitivity for detecting changes in the surface mass, as expected for observing a chemical reaction. Recent publications [321, 322] have modeled the conditions for optimum sensitivity for these waves. Clever variations in the parameter space available with the various wave motions suggests a flexible and valuable tool is possible if these devices are understood more fully.

#### 4.5 **Photographic Emulsion Improvements**

The use of local probes to reveal information about crystal structure has had practical consequences for improved photographic emulsion sensitivity. The details of surfaces associated with crystal faces clearly are revealed with local probes. One AFM investigation made in conjunction with the University of Basel, Switzerland, and Ilford, Co. found a correlation between the sensitivity of silver iodide crystals and the types of crystal faces exposed. Once this was understood, a method to grow the desired crystal faces was found, resulting in an increase in the speed of their color positive film by an order of magnitude. The



new technology is known as Surface Modification by Atomic Resolution Terraces (SMART). This improved film is now commercially available as a product from Ilford.

## 5. FUTURE OPPORTUNITIES

Throughout the text, a number of opportunities have been mentioned, evident from the discussion on each topic. In addition, some speculation about the future is inevitably offered in stimulating scientific conversations. This section offers a collection of such information.

### 5.1 Future Research Directions for Local Probes (LPs)

LPs [323] have been used extensively for characterization and manipulation of solid state systems, especially on model systems that have been studied exhaustively. Significant challenges today are associated with processes and functions. An example involving processes is that of measuring the rate of electron transfer through an organic molecule. Measurement of the properties of material (characterization) appear to be linear with the perturbation applied (up to a threshold)—i.e., structure does not appear to be a strong function of voltages applied. However when measuring functions, this may be much different. Biofunctions depend on the environment in which the molecule is found; it takes only a small change in pressure, or hydration, or other conditions to change this. In working with biological systems, we are working close to the instability limits of molecular systems.

A coming world is that of nanopatterning. Self-assembly in a directed way is coming. One can even consider highly parallel STMs, say  $10^4$  in parallel. The mechanical part of the nano world needs more development. Electronics has developed to a far greater extent than has the mechanical world. We would perhaps expect spatial dimensions to a nanometer, or a picometer, with time. It is not clear whether these degrees of refinement will offer that much of an advantage right now, however. "Chemics" is a term used to describe mass transport controlled on a nanometer or even picometer scale. This could be a valid complement to electronics. Right now there is an interface mismatch, but what we have done with electronics we may well be able to do chemically. "Our wisdom is not just in atoms."

An area that could open up to physics is that of how to deal with large numbers (and here large numbers means  $10^{12}$  to  $10^{15}$ ). STM deals with the behavior of a single particle. We now need to learn how to deal with an ensemble. We can theoretically treat  $10^9$  molecules on a computer, but we don't yet know how to scale this upward another 3 to 6 orders of magnitude. Behavior of  $10^{15}$  particles is different from that of a continuum; control of the behavior of this many particles can be based on the behavior of a single molecule. Note that we each individually control some 150 to 200 pounds of material in a coordinated and rather graceful manner—an extreme example of the concepts illustrated here. A physics breakthrough might well be how to solve the many particle problem such as making a robot with complex motions. This is a major task.

The atomic resolution offered by local probes may be important for calibration, but the LP community is hypnotized too much by atomic resolution. Industrial advances are more likely on a larger scale. We should think broader and not restrict our studies to those of atomic resolution.

Quantum interference devices are too complicated for what they bring to the technical community.

### 5.2 Other Future Topics

Many views regarding the future of nanostructures were expressed in numerous conversations about the subject. Some transfer from activities in the nanometer community will take place through better control of conventional systems. As an example, we will inevitably see a more routine fabrication of  $0.2\text{ }\mu\text{m}$  T-gates. One may expect to see FIB fabrication of waveguides and tunnel diodes, where the insulation is provided by the FIB.

II-VI materials offer a potential advantage due to the low electron mass, but this advantage is negated by wide line widths caused by material variations. It is difficult to obtain high quality structures with II-VI materials. There currently are some high-level considerations in Europe regarding the opportunities offered by II-VI materials.

Three trends are foreseen and are the subject of scrutiny in workshops and research representing potentially unifying views of frontline physics. These three trends are 1) downscaling (nanophysics); 2) coherent phenomena (linear superposition of ground and excited states - quantum beat phenomena); and 3) information handling with massively parallel computation.

The Turing machine represents an early model for computation. Consideration of a "quantum Turing machine" involves the question: "Can we have a superposition of states for manipulating information?" Information theory has been separate from physics until now. It is postulated that the quantum Turing machine can do things more efficiently. Nature works on a different level from the manner in which we simulate phenomena. By developing these ideas, it may be possible to simulate nature much more efficiently and to see "classical behavior" arising from our understanding of quantum phenomena associated with computation. It is postulated that with a quantum Turing machine the factorization of a large number into its prime numbers could be determined. The extreme difficulty of doing this via presently known algorithms is the basis for a large number of secure strategies in use today; changing this picture would change a large portion of effort involving cryptographic coding and analysis.

The question of cryptography and the distribution of public keys by way of the quantum channel is under investigation. By restricting the information to that of single photon pairs passed in two directions security of the received information can be assured. This is now being accomplished by TELEKOM over a distance of a few kilometers. With the practical implementation of such concepts, the demand for ultrasensitive and reliable photodetectors becomes a priority research question. This represents a potential area of investigation and application for nanoscience.

Another useful concept to consider is that of the polarization of a photon. The polarization of a photon with respect to the two independent linear polarization vectors (x or y-direction, say) can be used as a bit of information. If the orientation of these directions is not known when received, it is not possible to get that information from a measurement of a single photon, because the polarization state adjusts to the measurement basis. If the directions are known, the polarization state becomes an additional bit of information that may be used in sending information to an informed party.

Quasi-molecular cellular automation is another concept of interest. This represents the response of "information cells" to neighbors in the presence of an external (typically optical) stimulus. Energy dissipation in the form of luminescence and charge transfer excitation and migration could be developed to be useful concepts for information processing. A specific cell (or molecular system) will not be affected by an optical driving field of given frequency unless neighbors are in specifically designated states that match the proper energy for transfer. An implicit assumption about the coherence length and time scales is critical for the information to be transmitted in a useful manner.

The subject of cellular automata is still a confused issue. It is difficult to see how molecules could do this in a deterministic way. An often discussed example is the "shift register." Can such an elementary device be made to work?

## 6. CONCLUSIONS

One conclusion is clear from a straightforward presentation of the material in this document: scientific and technical programs in European nanoscience/nanotechnology are strong. The subject is one of growing importance and emphasis. This subject is one that brings different disciplines together; many of the opportunities, both scientific and technological, are at the interface between two or more disciplines. One may refer to examples such as lithographic variations using alternative chemical etching processes, or sensors using living cells from biological specimens. Indeed, the "vision" of nanotechnology is a unifying concept for a great deal of frontier research that is being accomplished.

Secondly, there are many advancing frontiers associated with the field. It is not clear which frontiers will yield the most fruitful discoveries, as is most often the case with scientific discoveries. But the frontier has considerable potential to advance the continuing trends for information storage and retrieval. In addition, digital logic and the transmission of information will continue to advance with activities in this field. The wealth of sensors under investigation suggests a great variety of products for use as environmental monitors, quality control sensors for enhanced manufacturing capabilities, higher performance platforms (automobiles and land vehicles, aircraft, and undersea vehicles), and many other uses.

Perhaps most important is the realization that the nanoscience community is uncovering information that will make us see a world that we do not now even envision. With an improved view of the forces, limitations, and opportunities that may be controlled through intelligent application of the laws of physics, biology, and chemistry, many opportunities can be foreseen for producing new materials. These materials are the basis for new products, enhanced performance, and capabilities that may now be only envisioned. A futuristic field such as robotics, as it unfolds, will inevitably make use of a great variety of new ideas emerging from this frontier.

"Nano" is a highly attractive field for well-formulated objectives and advanced concepts. A concern expressed by many, however, is that the opportunities appear so evident that hype about the subject could attract practitioners bent on hypothetical postulates or excessive "salesmanship" without a realistic appraisal of the products of experimental research. Overselling a field can be as detrimental as overly criticizing a field. Ultimately, too many researchers in a field lead to research conditions unable to fulfill advances for lack of suitable facilities as well as unemployment difficulties (some of which are evident today in technical fields).

As the community advances this fascinating field of miniaturization, it would do well to continually subject itself to self-appraisal for the long-term health and welfare. The behavior of materials having properties at variance with bulk materials, and behaving beyond the well-explored world of single molecule properties, is one that will take years to understand. It is complex beyond the known fields of macroscopic behavior and atomic/molecular behavior. Patience and perseverance will be needed to mine the benefits of this research and development endeavor.

Many of my colleagues in Europe expressed the following opinion: we should not churn our programs with rapidly changing expectations and directions, but rather set solid goals that can be sustained over periods suitable for the job at hand. That advice should be heeded for the enhancement of this fascinating subject. Many thanks, again, to the highly competent scientists who made this exposition possible.

## ACRONYMS/GLOSSARY

2-D	Two Dimensional
2-DEG	2-Dimensional Electron Gas
AES	Auger Electron Spectroscopy
AFM	Atomic Force Microscope
AFS	Atomic Force Spectroscopy
ALG	Advanced Lithography Group
ATR	Attenuated Total Reflectance
BEEM	Ballistic Electron Emission Microscopy
BMFT	Bundes Ministerium für Forschung und Technologie
CAMEL	Chalmers Advanced MicroElectronics Laboratory, Sweden
CEA	Commissariat a l'Energie Atomique
CEMES	Centre D'Elaboration de Materiaux et D'Etudes Structurales
CNET	Centre National d'Etudes de Télécommunications
CNRS	Centre National de la Recherche Scientifique (the French: National Science Foundation)
CSF	Compagnie Generale de Telegraphie, Sans Fil (= "without wire")
DFG	Deutsches Forschung Gemeinschaft
DFM	Dynamic Force Microscopy
DIMES/S	Delft Institute for MicroElectronics and Submicron Technology/Submicron
DLTS	Deep Level Transient Spectroscopy
DM	Deutsch Marks
DNA	Deoxyribonucleic Acid
DRAM	Dynamic Random Access Memory
EBIC	Electron Beam Induced Current
EC	European Community
ECR	Electron Cyclotron Resonance
EDX	Energy Dispersive X-Ray Analysis
EELS	Electron Energy Loss Spectroscopy
EPR	Electron Paramagnetic Resonance
EPSRC	Engineering and Physical Sciences Research Council
ESCA	Electron Spectroscopy for Chemical Analysis
ESPRIT	European Strategic Programme for Research and Development in Information Technology
ETH	Eidgenoessische Technische Hochschule, Zürich
FIB	Focused Ion Beam
FIMBE	Focused Ion Beam Molecular Beam Epitaxy
FKE	Austria: Institute for Solid State Electronics
FMRT	Federal Ministry of Research and Technology, Germany
FOM	Fundamental Research in Materials, Sponsoring agency in The Netherlands
FSU	Former Soviet Union
FTIR	Fourier Transform Infrared
FTZ	Telekom Forschungs- und TechnologieZentrum
FWFH	Austrian equivalent of the NSF
HEMT	High Electron Mobility Transistor
HREELS	High Resolution EELS
IFH	Institut für Hochfrequenztechnik, Darmstadt
IMS	Ion Microfabrication Systems
IPGT	In-Plane Gate Transistor

ISFET	Ion-Selective FET
ISS	Ion Scattering Spectroscopy
JEOL	Japan Electron Optics Laboratories
JESSI	Joint European Submicron Silicon project
JJ	Josephson Junction
KFK	Kernforschung Zentrum in Karlsruhe
KSLA	Koninklijke/Shell-Laboratorium, Amsterdam
LB	Langmuir-Blodgett
LCR	Laboratory for Central Research (in Orsay)
LED	Light Emitting Diode
LEEDS	Low Energy Electron Diffraction
LIGA	Lithographic Galvanoformung Abformung
LMM	Laboratoire de Microstructures et de Microelectronique
LMM	Laboratoire des Matériaux Moléculaires (in Thiais)
MBE	Molecular Beam Epitaxy
MEMS	Micro-ElectroMechanical Systems
MESA	MicroElectronics, Materials Engineering, Sensors and Actuators
MESFET	MEtal Semiconductor Field-Effect Transistor
MFM	Magnetic Force Microscopy
MINAST	Micro and Nanosystems, ETH, Zürich
MISFET	Metal-Insulator-Semiconductor Field-Effect Transistor
MMIC	Monolithic Microwave Integrated Circuit
NFOM	Near Field Optical Microscopy
NFWO	Nationaal Fonds Voor Wetenschappelijk Onderzoek (the "Belgium NSF")
NFR	Natural Sciences Research Council, Sweden
NPL	National Physical Laboratory
NUMBERS	Nottingham University Molecular Beam Epitaxy Research Syndicate
NUTEK	National Board for Industrial and Technological Development, Sweden
OMCVD	OrganoMetallic Chemical Vapor Deposition
PDI	Paul Drude Institut für Festkörperelektronik
PHANTOMS	PHysics AN Technology of Mesoscale Systems
PL	Photoluminescence
PMMA	Polymethylmethacrylate
PRL	Physics Review Letters
PSI	Paul Scherrer Institute, Switzerland
PTFE	Polytetrafluoroethylene
QCM	Quartz Crystal Microbalance
RHEED	Reflection High Energy Electron Diffraction
RTD	Resonant Tunneling Diode
s-n-s	Superconductor-Normal-Superconductor
SAM	Scanning Auger microscopy
SAW	Surface Acoustic Wave
SCALPEL	Scattering with Angular Limitation in Projection Electron Lithography
SEED	Self Electro-optical Effect Device
SELS	Spectral ellipsometry
SEM	Scanning electron microscopy
SERC	Science and Engineering Research Council (in Great Britain; renamed 1 April 1994 to the EPSRC)
SERS	Surface-Enhanced Raman Spectroscopy



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SFB	Sonder Forschungs Bereich
SFM	Scanning force microscopy
SFr	Swiss Francs
SFTIRM	Scanning Frustrated Total Internal Reflection Microscopy
SHG	Second Harmonic Generation Spectroscopy
SIMS	Scanning Ion Mass Spectrometry
SMART	Surface Modification by Atomic Resolution Terraces
SOM	Scheikunde Onderzoek der Materie, The Netherlands
SOM	Austria: Society for Microelectronics
SPM	Surface Plasmon Microscopy
SRAM	Static Random Access Memory
STEM	Scanning Transmission Electron Microscope
STM	Scanning Tunneling Microscope
STL	Scanning Tunneling Luminescence
TDS	Thermal desorption spectroscopy
TELEKOM	Germany: National Telecommunications Company
TEM	Transmission Electron Microscopy
TFR	Research Council for Engineering Sciences, Sweden
TUV	Technical University of Vienna
UHV	Ultra High Vacuum
UPS	Ultraviolet photoemission spectroscopy
XPS	X-Ray photoelectron spectroscopy
YBCO	Yttrium Barium Copper Oxide

## **Appendix A**

### **LABORATORIES VISITED**

Brief comments about the laboratories visited are included here along with information about individuals to contact at each of these organizations. It is hoped that this information will be helpful to others exploring potentially cooperative research programs as well as searching for a collegial exchange of information.

#### **A1. AUSTRIA**

##### **A1.1 Technical University of Vienna, Vienna**

The Technical University of Vienna (TUV) has approximately 23,000 students with five faculty: 1) Natural Sciences (Physics, Chemistry, Math, and Informatics); 2) Electrical Engineering; 3) Mechanical Engineering; 4) Architectural Engineering; and 5) Industrial Engineering. Future directions and emphasis seems to favor splitting the Natural Sciences faculty (which is now too large) into two faculties, where Mathematics and Informatics will split off into a new organization.

There are about 30 Ph.D. degrees in physics per year, and 50 in Electrical Engineering. Ten percent of the E.E. degrees are in the area of micro/nanoelectronics. Funding for research comes largely from the FWFH (full name not obtained; this is the Austrian equivalent of the NSF).

Professor Erich Gornik moved from the Walter Schottky Institute in Garching, Germany to TUV approximately one year ago. He is currently the President of the Society for Microelectronics (SOM) at TUV and the Head of the Institute for Solid State Electronics (FKE). The FKE is a collection of faculty within the university having common interests, and conducts a number of programs funded by the SOM in areas of nanoelectronics, optoelectronics, and optical spectroscopy. The SOM function is a non-profit organization with no personnel, and acts to allocate approximately \$1 M/yr in the areas of ion beam lithography and the Microstructure Center at TUV (these funds do not typically pay faculty salaries, which TUV pays). These funds are largely (90 percent) from the government, with 10 percent from industry. A board overseeing the functions of this society consists of five university and two industry representatives. Professor Gornik's research prior to arriving in Vienna involved characterizing quantum wires with magnetotransport measurements. Additional research of interest to him involved laser diode surface mode emissions and frequency shifting of diode laser emissions. Recent work involves tunneling processes between multiple quantum dots.

Since Prof. Gornik's arrival some 250 m<sup>2</sup> of clean rooms have been constructed along with a number of laboratories. Emphasis will be largely in semiconductor lasers as well as quantum dots, wires, etc.

Professor Wolfgang Fallman is Vice President of SOM. He has been involved with advancing the state-of-the-art of ion beam lithography for many years, and collaborates closely with Dr. Hans Loeschner, Executive Vice-President of the Ion Microfabrication Systems (IMS) organization located a few miles away from TUV. IMS is devoted to the design and oversight for construction of ion beam instruments; it has been in existence since 1985, and has had a total of \$25 M invested at the present time (with a current

number of 20 employees). Dr. Guenther Stangl is a chemist pursuing the development of new resists associated with ion beam lithography.

An interesting overarching philosophy discussed at TUV involved the need to go to lower voltages in electronic devices. This is being driven largely by the need for lower power consumption, which, of course, depends on the square of the voltage. Consumer electronics with battery-driven power sources is expected to be a dominant factor in advances foreseen. We need  $10^6$  kT of energy to store and read information today, whereas nature has figured out how to do this with  $10^2$  kT (figuring the brain capacity and power expended). In this respect, opinions were offered that we are doing too many mainstream research projects and too few of an innovative nature. "The risk is not there anymore." We produce many more papers but nobody does anything with them anymore. This is a consequence of too many scientists creating too much pressure on the system (one estimate suggested a factor of four too high; this is only an opinion offered).

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## A2. BELGIUM

### A2.1 Katholieke Universiteit Leuven, Leuven

The Katholieke Universiteit Leuven is a large university of 30,000 students and a fragment of the former 45,000 student university. In 1968 the larger united university was split based on language preference into the northern Flemish (Dutch-speaking) community and the southern Walloon (French-speaking) community. The French-speaking 15,000 students moved from Leuven (accent on the first syllable) 20 km south to Louvain (accent on the second syllable). Visitors to Leuven or Louvain would do well to recognize the competitive atmosphere involving these institutions.

Nanostructures are of interest in the Physics Department at Katholieke Universiteit with programs of Dr. Chris van Haesendonck (solid state physics in general, local probes and their use in fabrication as well as characterization, transport phenomena in nanostructures) and Prof. V. V. Moshehalkov (a recent transplant from Moscow State University with interests in phenomena involving nanostructures with superconducting materials).

The university budget is part of the 55 percent national university budget divided to the Dutch-speaking universities (additional universities in Brussels, Ghent, and Antwerp equal in numbers to that in Leuven). Research funds within the University (20 percent of the total budget) are allocated internally. Additional sponsorship may be obtained from 1) the Nationaal Fonds Voor Wetenschappelijk Onderzoek (NFWO, the "Belgium NSF"), 2) initiatives in research at the national level from the Prime Minister's office, and 3) from the European Community (EC) programs in Brussels (represented in this field as ESPRIT).

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### A2.2 Phantoms and the Institute Microelectronics Center (IMEC), Leuven

The Institute Microelectronics Center, located in Leuven, Belgium, was formed in January, 1984 to stimulate transitions from academia and research laboratories into the commercial sector of Belgium. It is supported by the Flemish Regional Government of Belgium. Approximately 350 people are on the IMEC payroll; counting students, visitors, temporary hires, etc., about 500 people occupy the facility which exists adjacent to some of the buildings of the Katholieke Universiteit Leuven.

The total funding of IMEC is about \$50M/year, with about half of that coming to IMEC from a variety of sources, including industry, services, and training to industrial components, bilateral R&D agreements, ESPRIT, and the NFWO (the Belgium "NSF").

There are three divisions at IMEC:

- 1) VLSI Systems Design methodologies, primarily to design software with an emphasis on signal processing;

- 2) Materials and Packaging, involving microsensors and circuits, solar cells, multi-chip modules, physico-chemical analysis, and electrical characterization; and
- 3) Advanced Semiconducting Processing Division, which deals with advanced CMOS processing and a pilot line for this function. The various research functions at IMEC are of considerable interest for the electronics industry in Belgium.

The primary reason for the visit to IMEC, however, was to learn about a European Community (EC) initiative with the title: PHysics AND Technology of Mesoscale Systems (PHANTOMS). This initiative started two years ago with a three-year \$1M contract from ESPRIT to IMEC. Renewal of this effort is currently under consideration since the contract concludes at the end of 1995. In this regard, ESPRIT is currently concluding its "3rd framework," with the 4th framework beginning in 1995. Renewal of these EC programs also involve review and reorganization efforts. The EC has other such contracts such as one in Molecular Electronics. In the central offices of the EC, agreements are reached as to the boundaries of the various coordinating efforts such as that between PHANTOMS and Molecular Electronics.

The overall purpose of PHANTOMS is to stimulate interaction among the multiple European research communities involved with research related to the physical properties of mesoscale structures. It initiates a number of networking opportunities involving research coordination, information dissemination, training of researchers, short exchange programs, international links, and industrial connections. A workshop is held once per year at which technical papers are presented and planning sessions are held.

There are 30 full members of PHANTOMS and 32 associate members. The primary difference between full and associate membership is that the full members have their cost of travel to workshop meetings covered. The membership currently consists of representatives from the following countries (some omissions due to incomplete information available at the time of discussion): United Kingdom (10); France (10); Germany (17); Denmark (1); Belgium (4); The Netherlands (4); Israel (1); Greece (1); Ireland (1); Italy (2); Spain (2). There are a few associate member of Japanese companies located in Europe.

PHANTOMS funds are used to support workshops and the cost of members attending workshops, exchanges of personnel, a brochure, a newsletter, database introduction and maintenance (of abstracts of papers) for access by members, an electronic bulletin board for members, and salaries at IMEC associated with administering the program (the equivalent of one full time professional plus secretarial support).

The newsletter is the most visible product of PHANTOMS, published about six times per year. There are currently 2000 individuals on the distribution list for this newsletter worldwide, with about 500 copies to the U.S., 400 to Japan, and the remainder to various locations in Europe. The newsletter consists of various technical overview articles involving mesoscale physics, editorials and opinions, membership information, announcements of meetings and conference, and some information about new publications.

Overall the PHANTOMS efforts appears to be an attractive way to provide interaction and coordination of programs in the various European nations. Its short history has managed to gain considerable interest among its membership; it was not anticipated that more than 35 laboratories would be interested when it was first formed. Its effectiveness will become more evident as the program continues, but its auspicious beginning appears to be very favorable for those participating. Dr. Mark van Rossum is the coordinator for the PHANTOMS program.

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### A3. FRANCE

#### A3.1 Centre D'elaboration de Materiaux et D'etudes Structurales, Toulouse

The Centre D'Elaboration de Materiaux et D'Etudes Structurales (CEMES) in Toulouse, France, is a laboratory of about 150 researchers, a unit of the French "National Science Foundation," CNRS. The laboratory has had a focus of studying material properties from its inception. The foundation for the laboratory is a 1 MeV electron microscope built in the 1960s used for diffraction studies on crystal structures. A more recent version of this instrument at 3 MeV is used today for many continued studies.

Drs. Christian Joachim and Jean-Pierre Launay head a group in molecular electronics, and J. Beauvillain heads a group in microscopy and surface analysis. The individuals responsible for the CNRS program in molecular electronics have an overall program of some 30 researchers, 15 of whom are in the CEMES laboratory located in Toulouse (the rest are elsewhere in France).

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#### A3.2 Commissariat a L'energie Atomique (CEA), Gif Sur Yvette

The Condensed Matter Research Department at CEA has about 600 people. Two separate groups within this Department are active in very different phases of the subject which is generally classed as "nanoscience." One of these is a solid state physics group headed by Dr. Michel Devoret. This group has examined the coulomb blockade effect extensively. The Molecular Chemistry group was, until recently, headed by Andre Barraud. Within this group is the Laboratory of Organized Molecular Systems, formerly headed by Dr. Andre Barraud ("half-retired"), and is now headed by Dr. Annie Ruaudel-Texier. This group is exploring the properties and utility of Langmuir-Blodgett (LB) films.

Langmuir-Blodgett films have been a focus at CEA, France, for many years [324-326]. Several well-controlled LB troughs are in operation for producing a great variety of films. The films have been used to develop resists for electronics, magnetic materials for memory devices, to understand electron transport mechanisms in molecular systems, along with a number of basic properties measured by laboratory instrumentation available. A principal goal of research today is to orient the molecular structures (with LB



films or with chemisorbed species) and observe the consequences of this orientation on the physical properties. Mechanisms used for fabricating interesting film properties include supramolecular interactions, which orient the molecules as they assemble into the films.

The magnetic materials show some interesting properties [327]. One such material prepared and characterized is a phenanthroline iron(II) thiocyanate complex which is ferromagnetic and has a Curie point near liquid nitrogen temperatures. As prepared it is a 2-dimensional material; some difficulty is noted with the stability of the current material. Another material (the structure of which was not clearly drawn, for obvious reasons, involves iron atoms bridged with several triazines (three nitrogen atoms in a five-membered ring). The Curie point for this material is apparently at 20° C. This work has been patented and is being pursued with a couple of companies interested in these properties. The work has not yet been published.

Other types of molecular systems used in these film structures include phthalocyanines, porphyrines [328, 329], thiophenes, TCNQ, along with binding groups such as acetylenes, silicate bridges, etc. to make 2-dimensional polymeric films. The potential utilization investigated includes the conductivity of these films and their use as possible sensors.

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### A3.3 Laboratoire de Microstructures et de Microelectronique, Bagneux

The Laboratoire de Microstructures et de Microelectronique (LMM) is one of the CNRS laboratories in France with 45 permanent people (and another five or so others). It carries out fundamental research as well as technology and device development. It is situated on a site of the French Telecommunications organization, which has additional electronics research laboratories and considerable interest in nanoelectronics developments. This association provides additional stimulation for the programs at LMM. The Head of LMM is Dr. Huguette Launois, who is also in charge of the CNRS program "ULTIMATECH." This program funds basic research in areas of microtechnologies, nanotechnologies, and optical properties of materials of interest for possible electronics and information technology applications.

Programs in fundamental research include efforts in Wigner crystallization, GaAs/AlGaAs superlattice formation and characterization, phase coherence, resonant tunneling, single electron device behavior, quantum dots and wires, and microcavities for optics. Technology programs involve e-beam fabrication, X-ray lithography, focused ion beam fabrication, STM/AFM/SNOM, MBE, etc. Device efforts include electro-optic structures, short gate HEMTs, single electron transistors, and InP heterojunction bipolar transistors. This laboratory in conjunction with the nearby laboratory in Saclay claim to have made the first single electron transistor, and regret not having given it more publicity. Bernard Etienne is very active in single electron effects and resonant tunneling; Dominique Mailly has considerable experience with superconducting phenomena such as residual magnetic fields. Y. Chen and F. Rousseaux are quite active in optimizing patterns with X-ray lithographic methods.

Overall, the laboratory has a broad and extensive capability to fabricate and characterize nanostructures by many different means and with a wide suite of instrumentation. The JEOL 5D2U e-beam nanowriter produces 20 to 30 nm structures on a routine basis, and has a 10 nm beam for exposure. A Philips e-beam instrument at 200 kV can pattern a 5 mm disk with 8 nm resolution patterns on aluminum fluoride with 16 bit position precision. X-ray masks have been made extensively, and form a substantial component of their research program. A gallium 30 kV focused ion beam (FIB) can deliver a 50 nm beam for FIB etching. Ion implantation facilities are available for use at neighboring CNET facilities.

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### A3.4 Thompson CSF, Orsay

Thompson CSF is an industrial firm which is mainly concerned with consumer electronics. "Thompson Inc." was originally formed from proceeds of a U.S. patent associated with commutators for motors more than 50 years. It merged with "CSF" (Compagnie Generale de Telegraphie, Sans Fil = "without wire") in the 1950s/1960s. Thompson-CSF bought RCA from GE in 1987.

About 10 percent of sales is redirected back to research, most of which stays in the division responsible for the sales. A small percentage of this research money supports the Laboratory for Central Research (LCR) in Orsay. This laboratory has about 300 people total with seven research groups: 1) Magnetism, 2)

Chemistry, 3) Electronic Components, 4) Optics, 5) Applied Opto-electronics, 6) Man-machine Interface, and 7) Physics. Nanostructures are examined in the Physics group, which has subdivisions of a) analysis, b) epitaxy, and c) polysilicon transistors for displays. Dr. Emmanuel Rosencher is head of the Physics group, and Dr. Borge Vinter is a theoretician supporting the programs especially those involving nanometer structures.

The physics programs involve quantum wells, intersub-band transitions, and IR properties of quantum wells, all with a vision of generating applications to IR detectors in the 3 to 20 micron region (8 to 12 is of most interest). Detector arrays are of some interest, and voltage tuning of detectors to different wavelengths is also of interest. Instrumentation for the fabrication of the materials for the efforts includes high quality MBE machines (a Varian => EPI, a Riber, and a new VG in which the 3" x 2" or 1" x 4" wafer is horizontal and injection occurs from the bottom).

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### A3.5 L'ecole Normale Supérieure, Paris

Academic research generally is generally supported within the university, at least for many faculty in France (observations of one faculty member). However, the university does not have support for postdoctoral fellows. Outside funding must be obtained for postdocs, equipment, and for travel. Potential sources of outside funding include Thompson CSF, CNET, and ALCATEL. The mode of operation in many French universities, as in this one, is that of a professor with a few students. Some individuals here are concerned when they have as many as three Ph.D. students; that represents a substantial load for a professor as each works very closely with the students.

The Department of Physics (150 to 200 permanent positions, of which a third are academic staff) graduates about 20 Ph.D.s per year. There are four rather independent "labs" within the department: theory, astronomy, atomic physics, and solid state physics, with the solid state physics component (the smallest of the four) having 25 to 30 members.

It was noted that there are very few "electrical engineering" departments in France. Such departments are considered critical for appropriately transitioning solid state physics into fields that use it in information technology applications.

Dr. Gerald Bastard is an employee of the CNRS located in the Solid State Group in the Department of Physics at the L'Ecole Normale Supérieure. French universities are incorporating a number of CNRS positions to strengthen the universities' teaching functions. Thus, Dr. Bastard now teaches approximately 60 contact hours during a year. He contributes a strong theoretical approach to predicting the behavior of heterojunction materials. Magneto-optic effects have been the subject of earlier investigations, and more recently work with Wannier-Stark states have been shown to give most useful devices for use as optical modulators. These devices are being introduced with the French CNET government telecommunications organization with efforts of Dr. Paul Voisin, another CNRS employee in the same department. This group has found collaborations with IBM, Yorktown, to be fruitful in the past.

This Paris group has no capabilities for preparing materials on site, so all experimental measurements must be done with samples obtained from IBM, AT&T, Thompson CSF, and elsewhere.

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**A3.6 Laboratoire des Matériaux Moléculaires, Thiais**

The Laboratoire des Matériaux Moléculaires (LMM) in Thiais is one of the CNRS laboratories in France devoted to pursuing molecular phenomena. Prof. Francis Garnier, whose interests include molecular conductors and organic molecules/complexes for electronics, has been head of most of the laboratory efforts for a number of years. Dr. Denis Fichou heads a group associated with the synthesis and characterization of oligomers and their possible applications for electronics. This laboratory was the first to report organic thin film field effect transistors. It currently has considerable activity associated with the electronic and optical characterization of organic materials. Mobilities of organic conducting polymers, for example, are measured by observing the current-voltage curves through an organic conductor acting as the charge carrier region of a transistor. Typical mobilities observed for thiophene oligomers, for example, are around  $10 \text{ cm}^2/\text{V-s}$  on single crystal material, but  $10^{-2}$  to  $10^{-7}$  for organic films. With substituents attached, the mobilities of these films can be increased to about  $0.2 \text{ cm}^2/\text{V-s}$ . There is some hope of orienting the molecular units in these films to improve mobility. Also electrochemical synthesis is envisioned as a way to introduce additional variations.

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**A3.7 Institut D'électronique et D'microélectronique du Nord, Villeneuve**

Institut D'Electronique et D'Microelectronique du Nord in Villeneuve has been recently formed from a combination of three separate organizations formerly near the current site. A new building was completed at the end of 1993 and was occupied early this year to place the individuals under one roof. The organization has about 300 people, including 140 permanent researchers (130 Ph.D.s). Five organizational

units are 1) Solid State Physics (III-V materials, superconductors, polymers, silicon, chalcogenides); 2) Microelectronics (silicon and III-V materials dominate: analog circuits, CAD); 3) Optoelectronics (photodetectors, modulators, integrated circuits, planar waveguides); 4) Acoustoelectronics (mixed circuits, sensors, ultrasound, sonar); and 5) Sensors for microwaves (microwave imagery, hypothermal detection - e.g., for tumor detection).

Facilities in this impressive new building include 1000 sq. meters of clean rooms, two MBE machines, ESCA, e-beam instrumentation (Cambridge EBPG 5HR => Leica with a 50 Å beam size, 250 Å size for writing), ion implantation/FIB with gallium, STM/AFM (UHV and in air), with additional instrumentation contemplated. This laboratory is expected to be a main (if not principal) site for III-V research in France. Silicon research is largely situated in Grenoble. Some of the objectives driving research here include the need for anticollision radar and for temperature sensors that may be used in health care.

The programs in this organization are clearly just getting under way. Although the individuals have all had considerable experience with programs pursued in the past, it is clear that future directions are being formulated as these individuals become comfortable in their new organization and physical surroundings.

It is also clear that the country has intended this site to be a major focus for many of the activities associated with nanoelectronics.

Dr. Michel Lannoo is head of the Materials and Microstructures Group (one of the group titles before a recent reorganization—pieces are still falling into place for this organization; this obviously includes solid state physics). He also heads a 10-person theory group, interested in nanoparticle behavior, epitaxial growth, porous silicon, and superconductor behavior (e.g., fullerene superconductor theory). Experimental physics includes efforts in defects in semiconductors, ESR, STM, and organic films as insulators on semiconductors. Silicon microelectronics here includes simulation of processes and devices (in three dimensions), behavior of materials such as porous silicon, and quantum effects.

Dr. Didier Lippens heads a "Quantized Component" group, interested in confined structures and their behavior/utility. Capabilities include 3-D modeling of transport behavior in confined semiconductor structures. Structures such as quantized directional couplers [330] are being modelled with the intention of fabricating these at some future date. Recent calculations comparing a self-consistent Schrodinger-Poisson code with the common Thomas-Fermi screening model have been applied to double quantum well configurations giving good agreement with experimental data. In this case, the experimental structure involved three InGaAs layers for a well and two AlGaAs layers for the barriers, all on GaAs.

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#### *A3.7.1 Laboratory Not Covered, But Personal Interaction*

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### **A4. GERMANY**

#### **A4.1 The Walter Schottky Institute, Munich**

The Walter Schottky Institute was founded in 1986 as a research institute for semiconductor research. It was funded initially by a joint venture involving Siemens and the Bavarian Ministry of Education. The equipment was purchased by the Bavarian Ministry, and the building was purchased by Siemens, costing a total of 17 M Deutschesmarks. It was financed for five years whereupon the Technical University of Munich became responsible for the finances (and the 17 M DM was returned to Siemens). The laboratory became operational in 1989. It is intended to enhance transitions between basic research and industrial production.

The total budget is approximately 2.2 M DM/yr, supporting a total of 60 people. Twenty positions are supported by the government (Federal Ministry of Research and Technology, FMRT), including three secretaries, seven technicians, and ten research assistants/post doctoral fellows. A major portion of the outside funding comes from Siemens (500 K DM/yr). Another significant portion comes from the FMRT in Bonn.

Some concern was expressed that higher-level enthusiasm is generating a large number of programs for heterojunction materials. Some 30 MBE machines must be operating in Germany now. The concern is that excess enthusiasm for the research opportunities here may result in disappointment at a later date if the requirement for this number of systems is not realized. Alternatively, there may be a number of duplicative efforts.

The building has a large suite of clean room facilities for preparation and examination of the materials used in the Institute.

There are three chair positions:

- 1) Guenther Weimann, working mainly in III-V materials, primarily GaAs, is currently the Director of the Institute;
- 2) Gerhard Abstreiter, working with SiGe and near-field optical microscopy; and
- 3) Peter Vogl, a theoretician involved with band theory and transport mechanisms.

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#### A4.2 Technical University at Munich

The research group of Professor Fred Koch in the Physics Department has been pursuing the subject of porous silicon, a material that luminesces by way of a mechanism which is as yet undetermined, although several mechanisms have been proposed.

Dr. Vesselinka Petrova-Koch was available during the visit, but Professor Fred Koch was not. We were able to discuss the subject in detail with researchers in the laboratory and with Dr. V. Petrova-Koch.

A laboratory involved with fabrication and measurement of nanostructures can benefit by spectroscopic measurements that characterize the energy levels of the materials produced. Professor B. K. Meyer has built an impressive laboratory for materials characterization. Some of these techniques are mentioned below:

- Optically detected magnetic resonance is used to examine defects in diamond, gallium nitride, CdTe, and other semiconductors.
- Cyclotron resonance is used to obtain the band structure, using a carbon dioxide pump. Mobilities in zinc telluride at 1.5 K have approached  $800,000 \text{ cm}^2/\text{V-s}$  in some of the materials made here.

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#### A4.3 University of Munich, Munich

This laboratory is in the department of Physics at the University of Munich. It is concerned mainly with the fabrication, characterization, and theory of arrays of quantum dots and wires. Professor Kotthaus is a Ph.D. graduate of the University of California, and interacts with the Santa Barbara group often. The Santa Barbara group is strong in fabrication of nanostructures, which complements the strengths of characterization and theory at the University of Munich.

The characterization of these arrays is largely by spectroscopic means. The laboratory boasts of its ability to take spectra at any frequency between d.c. and the ultraviolet. This is accomplished by two main systems, one a microwave system from 8 to 18 GHz with frequency multiplication capable of producing harmonics up to 300 GHz. The other is an IR interferometer using a bolometric detection which operates from 300 GHz (one mm wavelength) to approximately one micron. The additional portions of the electromagnetic spectrum are covered with conventional methods.



The laboratory concentrates on electrically tunable devices with quantum wires and dots. The advantage of electrically tunable devices is clear. Depletion effects are the most common way to obtain such tunability.

Sponsorship of the research involves over ten different organizations, including the Deutsche Forschungsgesellschaft (50 percent of support), the Volkswagen Science Foundation, The Ministry of Science and Technology, etc. There are about 40 people in the laboratory (including 15 graduate students) and the resources amount to about 1 M DM/year. The university pays for 6 or 7 assistants, 3 engineers, and one secretary. Even Japanese TELEKOM (NTT) is funding one student! The department graduates some 40 Ph.D.s per year in physics.

High magnetic fields are used effectively to measure the lengths and/or distances of the structures, as the diameter of carriers in the various Landau levels are fairly well defined in these materials.

Some interesting views involving self-assembly were expressed. Several years ago, self-assembly was taken to be a dream. Now, several important systems have been fabricated with self-assembly, including Molecular Beam Epitaxy (MBE) on strained layers to obtain 20 nm clusters.

The job market was discussed as representing a concern, a theme which was repeated several times in various laboratories in Germany. There is concern that the graduates for the first time in a long time are not able to find employment in physics. There are serious discussions at higher professional levels attempting to decide if the number of graduates in physics should decrease or if the profession is valuable even to those who must undertake employment in a field other than their chosen profession. Views differ on this.

There was also some concern that the subject which has the name "nano-" attached is being oversold. There are many laboratories now working on GaAs and variations. In semiconductors it is a bandwagon. "Every high school wants its nano lab now." But there are so many other directions this research can take. We could be graduating the solid state equivalent of the "nuclear physicists" 20 years from now! "When money is tight, it forces you to think, and you get better ideas."

Views expressed include a feeling that in Germany there is not enough interaction between physicists and chemists, particularly in this field. Trying to learn about new materials from chemists and molecular biologists is a challenge. "We are too much within our own fields right now." However, interaction does not take place by institutionalizing it. What is needed are small flexible units for fluid movement into opportunities for research. Japan seems to make joint programs but they disassemble after 8 to 10 years. Sometimes our projects are too short.

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#### A4.4 University of Würzburg

This laboratory is focusing on a variety of phosphorous-containing materials such as InP, and is heavy in opto-electronic device development. There is considerable interest in lateral nanostructures in this

laboratory. For example, distributed feedback (DFB) lasers are made here with InP/InGaP materials (at 1.3  $\mu\text{m}$ ) and InGaAs/GaAs (at 1.0  $\mu\text{m}$ ).

Overall, the programs in this unit are supported at about 2 M DM/year. There are 10 to 15 sponsors, including the Deutsche Forschungen Gemeinschaft, Volkswagen Foundation, Telekom, and others. A significant amount comes from ESPRIT (about 1.1 M DM in a three-year program). The university supports one engineer, two technicians, and a secretary. A quality clean room is associated with the laboratory which is supported at 300K DM/year.

There are about 40 persons (including five permanent staff) supported annually by the programs here. A philosophy with the educational program is that students will do both fabrication and characterization, not one or the other alone. However for specialty fields such as magnetotransport or picosecond measurements, there are specialists since these measurements are currently too involved to expect student part-time participation in these areas. There are currently three Russian scientists in the laboratory.

A clear trend for future emphasis in the laboratory is toward in situ characterization. This introduces the rapid switching from fabrication to analysis, while avoiding contamination by sample transfer.

A splendid facility housing clean rooms, Molecular Beam Epitaxy (MBE), focused ion beams, microscopes, etching chambers, Scanning Tunneling Microscopy (STM), etc. demonstrates the state-of-the-art in fabrication and characterization needed for this field.

A focused ion beam (FIB) unit produces 30 nm beams (half width at half height). A feature of this unit is that the voltage may be varied from 10 to 150 keV with little change in the focus characteristics. Structure sizes of 20 nm have been fabricated by picking off the "tip" of the beam through gold on GaAs. The beam will use gallium to produce insulating areas through defect production. Additional materials in the beam will include silicon, beryllium, and gold. It has fields for magnetic deflection to select any of the beams desired. The beam will be used to form localized areas for photonics where combined atoms will form larger band gaps to form a wave guide in the base material. An advantage of FIB is that there are no proximity effects as is the case in electron patterning of resists.

Lithography capabilities allow addressing a one square nm area within a  $50 \times 50 \mu\text{m}^2$ . There is a 20 nm "stitching accuracy" between squares.

Future research efforts here are clearly looking at improvement in the fabrication and control of dot structures. Good possibilities exist for producing improved laser sources prepared in situ with electron beams, focused ion beam etching, DFB lasers, etc.

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#### **A4.5 Technische Hochschule Darmstadt**

The Institut für Hochfrequenztechnik (IFH) at the Technische Hochschule in Darmstadt is headed by Professor Dr. Eng. Hans L. Hartnagel. This "Fachbereich" (faculty group) consists of four professors

(Hartnagel - microwave electronics, Weiland - field theory, Kessler - radar, and Vlcek - antennas). Professor Hartnagel's own interests include heterojunction bipolar transistors (GaAs/AlGaAs, InGaAs/InP), HEMT structures, and MMICs. Objectives of this research are largely in optical communications and sensors at high temperatures.

A substantial program is funded by the Deutsche Forschung Gemeinschaft in the area of measurements for automobile engines. This funding involves several million Deutschemarks per year over a period of 12 years. Members of the Electronics and Mechanical Engineering departments collaborate to measure the many detailed phenomena (temperature, pressure, air flow) taking part in the cylinders and turbines of engines, tires, and components of automobiles and aircraft. The low thermal conductivity of GaAs/AlGaAs along with the high Seebeck coefficient and the ability to integrate these sensors on a chip make this material attractive for such sensors. Additional funding is attracted from the Federal Ministry of Technology.

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#### A4.6 Telekom Forschungs- Und Technologiezentrum, Darmstadt

The Deutsche Bundespost was restructured in the last several years, resulting in a change in the name of this research center from Forschungsinstitut der Deutschen Bundespost TELEKOM to its present one (effective six months ago). The Bundespost now consists of 1) the postal service, 2) the postal bank, and 3) Deutsche Telekom. Some 150 researchers and a like number of technicians are located at this research center in Darmstadt. A similar number are also located in Berlin, which was formed with the coalescence of East Germany. Prof. Hesse is head of a 60-person research group in the Electronic-Photonic Support Division in the Research Branch of this Center.

Dr. Hans W. P. Koops at this center is instrumental in designing electron beam equipment. His background is one involving refinements to some of the highest resolution electron microscopes and in designing some advanced electron beam lithography instruments. He helped develop the "SCALPEL" principle to remove diffraction effects for electron projection lithography equipment, a process which is now being used in advanced instruments. This background involves understanding the multipole interactions and positions of the various correction fields to minimize the aberrations and limitations present in electron beam equipment.

That background of electron beam design is now being applied to the design of some remarkably different electron beam devices that are smaller than a few microns in several cases. The dramatic change in the scale of lengths retains the principles to be applied to this developing miniature field.

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#### A4.7 Tübingen University

The Institute of Physical and Theoretical Chemistry at Tübingen is oriented toward physical measurements largely for creating sensors associated with nanostructures and surface phenomena. Professor Wolfgang Göpel is the Department Head of this institute with some 35 people, including 6 to 7 professors. The institute graduates about four Ph.D.s per year.

Although not specifically oriented to nanostructures per se, the objectives of making sensors are closely related to the exercise of fabricating and understanding nanostructures, and this activity is thus included in the overview of activities related to nanostructure fabrication and characterization.

Chemical sensors for a great variety of molecular systems using many physical phenomena are under study here. Concepts such as the electronic nose are being pursued, along with collaborative efforts involving research in England.

Unique molecular interactions may be designed through modifications in molecular structure to be specific to designated chemicals. The design mechanism for this is being developed with considerable experience in this laboratory.

A recent book edited in this institute was noted: *Nanostructures Based on Molecular Materials*, edited by W. Göpel and Ch. Ziegler, VCH, New York (1992); ISBN 3-527-28416-8. A second book, authored a year earlier, consists of contributions from a number of countries other than the U.S.: *From Instrumentation to Nanotechnology*, edited by Julian W. Gardner and Harry T. Hengle, Gordon & Breach Science Publishers, Philadelphia (1991); ISBN 2-88124-794-6.

In the design of molecular sensors, it is clear that a wide variety of instrumentation is necessary to obtain sufficient information about the molecule-surface interactions. The instrumentation suite in this institute is impressive:

- X-ray photoelectron spectroscopy (XPS)
- Ultraviolet photoemission spectroscopy (UPS)
- Thermal desorption spectroscopy (TDS)
- Scanning tunneling microscopy (STM)
- Atomic force microscopy (AFM)
- Low energy electron diffraction (LEEDS)
- Scanning electron microscopy (SEM)
- Scanning Auger microscopy (SAM)
- Scanning ion mass spectrometry (SIMS)
- Energy dispersive X-ray analysis (EDX)
- Ion scattering spectroscopy (ISS)
- Auger electron spectroscopy (AES)
- Electron energy loss spectroscopy (EELS and HREELS)
- Spectral ellipsometry (SELS)
- Optical spectroscopies (FTIR, visible, ultraviolet, Raman)
- Attenuated total reflectance (ATR)

With these instruments, the institute is well equipped to examine in detail the phenomena associated with a desired sensor design, and to intelligently modify the interactions to obtain the desired results.

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#### A4.8 Max Planck Institute Fur Festkörperforschung, Stuttgart

Professor Klaus von Klitzing received the Nobel Prize in Physics in 1980 for his discovery of the quantum Hall effect. He has a large group at this institute (about 40 individuals), and is examining magnetotransport phenomena today, as well as some new areas such as coulomb blockade phenomena. Some feelings about the importance of the coulomb blockade were offered, indicating that "this is a big one." Research with this phenomenon should be directed at room temperature devices as well as their use for current standards. They represent a move beyond semiconductors. Fabrication efforts with focused ion beams have been undertaken in conjunction with the measurement exercises associated with transport phenomena of nanostructures.

The Max Planck Institutes are essentially "super graduate schools," where 80 percent of the scientists at these institutes have less than five years of residency. Only a very few remain in permanent positions at Max Planck Institutes. The Institute in Stuttgart has nine such professors, 100 Ph.D.s, and 100 students. Three principal areas pursued in Stuttgart include 1) chemistry, 2) theory, and 3) experimental work. The philosophy is one in which the very best scientists are selected and given their freedom to pursue research programs.

Views were offered expressing concern about the large number of researchers entering the field of epitaxial fabrication of heterojunction materials. Such equipment is not useful for studies of biological systems, for example.

Sponsorship by the Bundes Ministerium für Forschung und Technologie (BMFT) includes a group interested in III-V materials. In this sponsorship, a number of institutions (industrial and academic) are involved and meet every six months. One such consortium supports development of in-plane transistors (discussed below) and includes the following partners: Siemens, Daimler Benz, the Max Planck Institute in Stuttgart, the Fraunhofer Institute in Freiburg, the Paul Drude Institute in Berlin, and the Heinrich Hertz Institute. The collaborative meetings involving research institutes and industry appear to be inducing enhanced lines of communication and a bridge between research and industrial utilization.

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#### A4.9 University of Stuttgart, Stuttgart

Professor Günther Mahler is a theoretician whose views gravitate to possible trends for next generation fields of physics. Nanoscience is one of the many fields he considers, with broad observations supported with in-depth theoretical analyses.

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#### A4.10 Westfälische Wilhelms Universität, Münster

Professor Harald Fuchs is in the Physikalische Institut für Festkörper Physik (Solid State Physics) at this university in Münster. This university is the third largest in Germany, with 46,000 students. The group which Professor Fuchs is setting up is about one year old, and is continuing research programs initiated while Dr. Fuchs was previously at BASF, Ludwigshafen. His group is focusing on careful physical measurements on molecular materials using the tools available in solid state physics. The fabrication of "unconventional materials" involves the epitaxial growth of organic materials as well as the preparation of Langmuir-Blodgett films. Characterization is largely with scanning probes, with very good productivity demonstrated with these tools and organic films [331-336]. The laboratory is building an impressive suite of instrumentation, including three units for STM, three units for AFM, two near-field optical microscopy units, FTIR, Raman spectroscopy, second harmonic microscopy, LEEDS, Auger, Mass spectrometry and others.

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#### A4.11 Yoh. Gutenberg-Universität Mainz, Mainz

One program described in this newsletter is at the Institute for Physical Chemistry, implemented by a physics professor (Prof. Rabe) who occupies a chair in the Physical Chemistry Department. A second program exists with Prof. Ringsdorf, who, unfortunately, was unable to keep an appointment. Some research associated with Prof. Ringsdorf's group was discussed with Dr. Felix Kramer, a postdoctoral fellow.

There is a tradition at Mainz to have cross-disciplinary appointments. One-third of the chair appointments in the Physical Chemistry Department are of physicists. This is, of course, to stimulate cross-disciplinary interactions. The philosophy was expressed that the physicist makes careful measurements on molecular systems that only the chemist is able to prepare and characterize structurally. The need for mutual appreciation was expressed with pride. The nature of the program described here reflects that fact explicitly.

Professor Juergen Rabe has occupied the chair here for a year prior to occupying positions at a Max Planck Institute, the Technical University in Munich, and IBM Almaden. He is building a group dedicated to examining molecular interfaces at the solid state boundary layer. This includes studying 1) how the molecules organize, 2) how they interact with the substrate, 3) the dynamics of the processes, and 4) the electron transport associated with these molecular systems. A fundamental thesis to all of these efforts is "It only makes sense to study transport properties on well-characterized materials."

Scanning probe microscopy is the primary tool now used to examine the materials. Structural patterns caused by molecule-surface interactions demonstrate beautifully the experimental realization of the atomic picture which has been assumed for such interactions for years. The importance of an atomically flat substrate is emphasized for these studies. The programs seem to be moving from hydrocarbon systems to more complex molecular systems. This program is part of an ESPRIT consortium examining processing on a nanoscale.

Some information regarding program support was given. The university provides the professor's salary, space, initial set-up equipment, minimal personnel (1 to 3 engineers, depending on seniority, 1/2 to 1 secretary, one or two graduate students, and diploma students) and "running costs," amounting to about \$12,000 per year (operating costs). Overhead is not a cost allocated to any sponsor. Outside sponsorship pays for additional graduate students, postdoctoral fellows, technicians, equipment, and other staff. A graduate student's salary is approximately \$18,000 per year; a postdoctoral fellow's is about \$36,000 to \$50,000/year. The biggest sponsors for these programs are ESPRIT, the Ministry of Research and Technology, and the Israeli Foundation. Industrial interest is shown by industrial cooperative efforts associated with the Ministry of Research and Technology.

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#### **A4.12 Festkörperphysik, Technische Universität Berlin**

The Technical University of Berlin (formerly the Technical Hochschule) has approximately 30,000 students. This is strictly a technical university located in western Berlin, formed after WW II by the Allies. Humboldt University is located in the eastern portion of Berlin, with an additional 30,000 students, with strong programs in medicine, literature, Marxism, and Leninism. The Freie Universität Berlin (with 30,000 students) was founded in western Berlin as a counterpart to the Humboldt University, and has strength in linguistics, romanistics, medicine, biology, and a university hospital. With the unification of the two halves of Berlin, some attention is being given to clarification of the strengths of these three universities along with other nearby institutions.

The Physics Department at the Technical University of Berlin has six "subdepartments:" 1) Astronomy; 2) Solid State Physics; 3) Metal Physics; 4) Nuclear/atoms; 5) Theory; and 6) Teaching. The Solid State Physics subdepartment has a total of about 120 people, including students, and graduates approximately 15 Ph.D.s in S. S. Physics per year.

Prof. Bimberg is one of four full professors (and one "Associate Professor") in the Solid State Physics sub-department, with interests in the optical properties of nanodimensional cluster species as well as MOCVD processes with transition metal layered materials as well as semiconductors. Some of the interest in transition metals is for the purpose of providing semi-insulating layers for isolating devices, especially for growth in the third dimension. The group is also interested in high frequency optical detectors using absorption effects and interdigitated structures. Dr. Marius Grundmann is an "Ober Engineer," essentially the only assistant professor in the Solid State Physics subdepartment. His interests are largely in the optical properties of nanostructures, and he was present for the discussions (Prof. Bimberg was not available during the "vacation month" of August). The group works in close collaboration with Prof. Alferov at the Ioffe Physical-Technical Institute in St. Petersburg, Russia. Many of the samples characterized within this group are prepared at the Ioffe Institute. One of the ultimate objectives is to make lasers using the unique properties of quantum dot materials with low thresholds and sharp cathodoluminescence. The process of self-organization for fabricating large numbers of nanostructures through slight mismatches of lattice constants is being explored for the fabrication of quantum dots. The use of "V-grooves" is under study for the fabrication of quantum wires.

Funding for research in the group associated with Bimberg comes largely from 1) the Bundes Ministerium für Forschung und Technologie (BMFT), 2) the Deutsches Forschung Gemeinschaft (DFG; the German counterpart to the U.S. NSF), 3) the Sonder Forschungs Bereich (SFB) which is a special "big projects" program associated with the DFG, and 4) industry directly. There is a definite trend in funding

levels that will move the group into research associated with GaAs/AlGaAs quantum dots. The laboratory equipment available for research in this area includes two OMCVD machines, a 14 Tesla magnet, photoluminescence equipment, and calorimetric absorption spectroscopy equipment.

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#### A4.13 Paul Drude Institut für Festkörperelektronik, Berlin

The Paul Drude Institut für Festkörperelektronik (PDI) in eastern Berlin consists of about 75 people (half of whom are scientists). Professor K. Ploog is the Director of the Institut, having recently joined it from the Max Planck Institut in Stuttgart where he was associated with Professor von Klitzing. The organization was founded in January 1992, and it evolved from a portion of the Central Institut of Electron Physics (which consisted of 700 people a few years ago) which occupied the same building (among others) now occupied by PDI. The Central Institut effort in plasma physics was dispersed to other locations, including the Max Planck Institut in Munich. Other personnel changes were made, but not described in detail. The East German Academy of Sciences had 24,000 employees, of which a third found jobs at other research institutes after the reunification process. Industrial technical employees fared even worse, with 85,000 jobs decreasing to 15,000 after reunification.

One factor apparent when visiting Berlin (both the eastern and western sides) is that there has been considerable duplication of effort there during the past 40 years (two opera houses, two historical centers, etc.). Western Berlin funded its research institutes well, but now a more "realistic" level is being introduced. Eight laboratories formed a consortium to enhance the use of resources and minimize duplication of efforts in the immediate area. They include the following:

- 1) Forschungsinstitut für Molekulare Pharmakologie
- 2) Institut für Angewandte Analysis und Stochastik
- 3) Institut für Gewässerökologie und Binnenfischerei
- 4) Paul-Drude-Institut für Festkörperelektronik
- 5) Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie
- 6) Institut für Zoo- und Wildtierforschung
- 7) Ferdinand-Braun-Institut für Hochfrequenztechnik
- 8) Institut für Kristallzucht.

The Paul Drude Institut is organized into five groups: 1) Nanostructures (with MBE especially); 2) Optics, with emphasis on electron and phonon density of states along with analytical methods; 3) Transport phenomena, especially magnetotransport in a 2-dimensional electron gas (2-DEG), delta-doping,

and hot electron transistors; 4) Solid state acoustics (with SAW devices among other thrusts); and 5) Analytical methods (X-rays, cathodoluminescence, SEM, Electron Beam Induced Current (EBIC), Deep level transient spectroscopy (DLTS), luminescence, photocurrent spectroscopy, time-resolved photoluminescence, etc.).

A focus of this laboratory involves III-V semiconductors. The laboratory is involved with the more basic aspects of research in the fields it pursues, with more applied aspects (closer to electrical engineering) being pursued at institutes such as the Heinrich Hertz Institut concerned with making devices such as surface lasers. Those aspects associated with nanostructures emphasize fabrication, with a significant interest in self-assembly methods for producing large numbers of nanostructures. Research in solid state physics involves vertical transport through heterojunction materials (inversion in 2-dimensional sub-bands, LEDs), Wannier states, Bloch oscillators (as modulators and SEED devices), etc. Funding for the efforts here are split approximately 50:50 between the Ministry for Research and Technology and the State of Berlin.

General conversations revealed the feeling that the term "nanoscience" is definitely oversold at the present time (particularly quantum wires and dots), and a careful assessment of the most opportunistic aspects should be considered. One problem associated with the field is that, in some cases, researchers are not careful with what they are measuring. This results in some unrealistic expectations and a loss of credibility. Further, results easily obtained at milli-Kelvin temperatures are discussed as though there is a possibility of achieving similar results at room temperature, which is unrealistic. Utility is unlikely from these materials through their room temperature properties. To maintain credibility, researchers should focus on parameters such as homogeneous size distribution, large numbers of nanostructures, and reproducibility of fabrication techniques.

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## **A5. GREAT BRITAIN**

### **A5.1 Cavendish Laboratory, Cambridge**

Cavendish Laboratory at the University of Cambridge is a historic laboratory that points to 26 Nobel Laureates who have worked there for extended periods. The Laboratory is devoted to research in experimental physics. With historical members such as Maxwell and Rutherford, the contributions from Cavendish Laboratory seem to pervade a great number of advances we take for granted today. The laboratory today has eight professors, 60 staff (for teaching and research), 200 additional researchers, 200 graduate students, and a number of undergraduate students.

Nanoscience and nanoengineering are active areas of research in at least three areas at the Cavendish Laboratory: 1) Semiconductor Physics, 2) Microelectronics Centre, and 3) Surface Science.

Semiconductor Physics is headed by Prof. Michael Pepper, who was one of the co-authors of the original paper demonstrating the quantum Hall effect. Dr. C. A. C. Jones works with Prof. Pepper. This group has approximately 60 people, including 4 to 5 faculty members. The group is responsible for

initiating the depletion method of side-wall gating in order to change the dimensions of the conduction channels with increasingly small channel width as a function of voltage on the gate. It was this technique used by the research group in Delft and Eindhoven, The Netherlands, to discover the quantized conductance at low temperatures.

The Microelectronics Research Centre at the Cavendish Laboratory has as its main mission the objective to move ideas from physics to devices. The director, Prof. Haroon Ahmed, is personally involved with a great variety of programs involving many of the 40 individuals working in this center.

The Microelectronics Centre is expanding, approximately doubling its floor space with an addition starting late this spring. There is considerable optimism about the intellectual and potentially practical opportunities offered in this field; it appears to be attracting some excellent students. Considerable thought is being given to the integration of sensors concurrent with the electronics on the same chip. That appears to offer a number of opportunities as this field expands.

Dr. Richard Palmer is head of the Surface Science section of the Cavendish Laboratory. His programs involve 1 to 15 students and postdoctoral fellows in areas of 1) surface modification, and 2) cluster physics with nanophase materials.

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### A5.2 University of Cambridge, Engineering Department

The Engineering Department at Cambridge University is headed by Professor Alec Broers, who has had considerable experience with fabrication of nanostructures using lithographic techniques. His interests (along with running a university) include analyses associated with the future systems for industrial production of chips. Dr. Mark Welland in this department is involved with using a number of local probe techniques to elucidate information at the nanostructural level [337]. Welland's group consists of approximately 14 people, 12 physicists and 2 engineers.

Instrumentation available in this combined group includes a 400 keV electron beam capable of fabricating 20 to 50 nm gold lines with 8 bit positioning (16 bit positioning is to be added soon) on a 5 mm wafer. A 40 keV scanning electron beam microscopy is available with 10 nm resolution for imaging. STM instrumentation at  $10^{-11}$  Torr is available with temperatures up to 800° C, along with Auger spectroscopy in the same vacuum chamber. Low temperature STM will go from 4.2 K to room temperature. A combined scanning electron microscope and STM is available for close examination of samples with both techniques [338]. Atomic force microscopy and magnetic force microscopy [339], [340] are available. A digital control system for STM and AFM has been designed and is generally available [341].

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### A5.3 Oxford University, Oxford

Oxford has several groups dealing with phenomena involving nanostructures. Dr. Colin Bain in the Physical Chemistry Laboratory is introducing the relatively new tool of sum frequency spectroscopy for studying the properties of thin organic films. This nonlinear technique gives spectral information identifying molecular species and additional information relating to orientation of the species under investigation. Dr. J. B. Pethica is involved with local probes, but unfortunately was not available during the period of these visits. Dr. Peter Dobson in the Engineering Science Department has found some novel methods of fabricating relatively monodisperse clusters using electrospray techniques. Professor Richard Compton is an electrochemist making use of micron-sized electrodes and rapid fluid flow to observe fast chemical reactions.

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#### A5.4 University of Glasgow, Glasgow

The Electrical Engineering Department at the University of Glasgow has a Nanoelectronics Research Centre. Programs in this center are carried out by professors in Physics as well as Electrical Engineering. A rather large grant of \$3.3M over a four year period from the SERC (now the Engineering and Physical Sciences Research Council, EPSRC) is one of the more substantial core support areas for this center. Other programs are supported by the European ESPRIT. Programs involving industry are welcome, and cost-sharing incentives are in place to encourage this type of interaction. There are about 15 academic staff and 60 research workers (students, fellows, and "research technologists") in the center. A research technician typically costs \$40 K/yr, and a graduate student \$15 K. Faculty do not pay their salary from research grants, although this is beginning to change with some recent encouragement to buy faculty time.

The center is divided into eight divisions: 1) Molecular Beam Epitaxy; 2) Optical phenomena; 3) Transport phenomena; 4) Device Modeling; 5) High Speed Devices; 6) Single Electronics; 7) Electron Beam Lithography; and 8) Dry Etching. The program support from EPSRC has undergone a shift in emphasis recently, where the majority of the future effort will be supported for the development of high-speed devices. This may be compared to some extent with the MMIC program in the states. Emphasis here appears to be on 94 and 140 GHz behavior and devices. Materials in the center have been largely III-V compounds and structures, although there is a decided shift and emphasis back to silicon.

Four professors are very active in publishing and leading efforts in the nanoscience area. These four held discussions along with several other researchers involved in the projects under way. The four professors are

- 1) John Davies (theory involving statistical fluctuations);
- 2) John Barker (theory involving device modeling);
- 3) Steve Beaumont (overall coordinator for the EPSRC program); and
- 4) Chris Wilkinson (etching phenomena and biological phenomena).

The Chair of the Department of Electrical Engineering is Prof. Peter Laybourn. Other professors, academic and research staff are active in this field; had a chance to talk with Richard de la Rue (optics), John Williamson (single electronics, quantum effects), Stephen Thomas (lithography), Nigel Cameron (FETS), and John Weaver (AFM).

The structure and functions of the sponsoring agencies was discussed and is of some interest. Sponsorship through the EPSRC is for basic research within England. The direction of the research is determined primarily by the proposal, and deviations from the original direction of the research should be minimal. In that respect, there appear to be constraints on the flexibility of such funding.

Programs funded through the European ESPRIT program are determined with a selected group of well known researchers acting as a board for such decisions. This group and representatives from the funded research groups meet quarterly at locations of those participating in the research. If the group finds a change in direction to be advantageous, such changes may be approved and implemented in the course of the program. In this respect, the ESPRIT programs offer some additional flexibility. Feedback from other researchers in different countries (gained subsequent to this initial discussion) suggest that a principal benefit of the ESPRIT programs is the interaction with good researchers elsewhere.

There was some feeling expressed that devices below 0.2 micron in feature size represent somewhat of a barrier. The reasoning is that these devices will approach 100 electrons per device. Fluctuations in performance at these levels will be sufficiently disruptive to make performance marginal. In order to obtain enhanced processing power, an alternative to smaller feature size is larger chip sizes. This may represent a more cost-effective way to proceed in the short run, and both paths should be explored.

With the last decade of research in nanodevices, it is becoming clear that many of the desired properties of nanostructures are associated with the behavior of defects. In many respects, there is a trend to look more closely at "dirty devices" because of the interesting behavior found there. Strained lattices, self-organization, defects having interesting transport properties, etc. all point to this as a general topic worth pursuing.

An example of an applied program was described involving FET design for satellite linkages. This program involved the construction of a 200 nm T-gate exposed with three layers of PMMA, each having a different sensitivity (a reasonably standard technique). With this device, 20 dB gain was observed from 41 to 47 GHz over three stages. Newer work using pseudomorphic HEMTS and 0.1 micron gate lengths will produce devices expected to operate at 94 and 140 GHz. A principal objective of this latter research is in support of collision avoidance devices and automatic toll registration on automobiles. These applications seem to be mentioned often at other laboratories throughout Europe.

The facilities at Glasgow include three electron beam machines capable of producing 10 nm beams (since the late 1970s), 12 nm beams (relatively new), and 2 nm beams (1987 procurement). The highest resolution machine is more complicated to use and most resists will not yield 2 nm inherently in the response of the resist. Thus this last machine has not stimulated as much use as the other two at the present time.

The current computer in use in the department is one involving 96 parallel processors with a peak performance figure of 224 MFLOPS. A prototype computer should be available in December of 1994 (with four processors initially) with the 601 Power PC, which has an individual processing capability of 35 MFLOPS. In a couple of years they are projecting the introduction of the 620 Power PC which is to be 10 to 30 times faster. The intent is to model such problems in six dimensions (coordinates and momenta in 3-D space). The Power PC is manufactured very close to Glasgow.



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### A5.5 University of Nottingham

The University of Nottingham Physics Department has a strong program in low-dimensional semiconducting structures called the Nottingham University Molecular Beam Epitaxy Research Syndicate (NUMBERS), which has been supported by the Engineering and Physical Sciences Research Council (EPSRC) in England for more than a decade. A broad spectrum of programs in the Physics Department focus on the properties of nanostructures. NUMBERS focusses on measurements in 2-dimensional electron gases (2-DEGs) with a strong component associated with transport behavior in magnetic fields. Additional phenomena associated with high frequency systems and phonon structures are included in the

program. NUMBERS has associated with it some 60 people with some 15 permanent academic staff, 20 Ph.D. students, and 15 postdoctoral fellows.

Several senior professors have strong programs of their own in this overall umbrella program. Professor Laurence Eaves is the Head of the program with a long history studying magnetic effects in 2-DEGs. M. Henini is an experimentalist associated with the production of leading material properties with the MBE facilities at the laboratory [342-344]. L. J. Challis is involved with phonon structures associated with 2-DEGs. Martin Chamberlain is involved with high frequency (up to the infrared) devices and systems.

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#### **A5.6 University of Birmingham**

Research at the University of Birmingham associated with nanostructures is largely in the area of molecular structures which are quite novel, with interesting properties in their own right. Professor Fraser Stoddart, Chair of the Chemistry Department, has a major program devoted to catenanes and rotaxanes, described in Section 2.5 of this report. These molecular systems have properties of "switching," which may provide piezoelectric or photochromic behavior of interest. Formation of these molecules takes place through molecular associations involving supramolecular interactions, and represents one aspect of many innovative and clever design techniques for new classes of materials [345, 346]. In many respects, the research undertaken in this laboratory represents an attempt to transfer knowledge and techniques involving self-assembly operating in life processes to more general molecular systems not found in life.

From success in using supramolecular interactions to form unique product structures, there are thoughts of forming autocatalytic systems (or self-replicating molecular systems) in which the products would depend on the presence of a product already in the reactant mixture. In this case, the product would depend on the seed originally present. This then would resemble cell reproduction and life processes, areas of future research.

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#### **A5.7 National Physical Laboratory, Teddington**

The National Physical Laboratory (NPL) is the English counterpart to NIST in the U.S. Dr. Al Franks is head of the Nanometrology Group in the Division of Mechanical and Optical Metrology at NPL. Also Dr. Margaret Stedman is well known for her work in measurements, which currently is being directed at instrumentation associated with nanometer dimensions. Several instruments and individuals are involved

with standards for measurements associated with nanometer fluctuations, and the limits of measurement at sub-nanometer dimensions [347, 348].

The background of this group is that of working with optical component for X-ray microscopy. Emphasis changed to precision measurements and positioning with the increased emphasis on nanometer science and technology.

This now includes measurements of surface roughness, which is quite important for industry. Several instruments have been built to map nanometer imperfections across a flat surface. Another aspect of these measurements, applicable to spectral measurements as well as position measurements, is a set of "amplitude-wavelength" principles. These are generally applicable when instruments are making measurements at the extreme of the capabilities for which they are designed. Standard metrology for STM devices is now in demand due to the large number of users wishing to know the limits of the instrumentation available.

The laboratory has various home-built instruments for the measurement of surface roughness. A "Nanoscope II" by Digital Instruments has STM, AFM, and Scanning Near-Field Optical Microscopy (100 nm resolution) capabilities. A major challenge for the standards group is to know the effect of a measurement with a local probe, since the observed image is a convolution of the object with the shape of the local probe observing the object.

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## **A6. THE NETHERLANDS**

### **A6.1 Koninklijke/Shell-Laboratorium (KSLA), Amsterdam**

Shell Research in Amsterdam is one of the few research laboratories associated with the Royal Dutch holding company, of which Shell Oil of the U.S. is one subsidiary. Research in this laboratory involved some aspects of self-assembly, which is a basis for fabrication of certain nanostructures. This visit was made to ascertain different aspects of motivation for investigating nanostructures, as well as to determine alternative tools that may have been used for their study.

The laboratory, known as the Koninklijke/Shell-Laboratorium, Amsterdam (KSLA) is located in downtown Amsterdam, and conducts research involving chemicals, engineering, and oil processing.

Motivation for the study of nanostructures is from two main applications of interest to the oil company: 1) emulsification of oil (e.g., for removal in case of an oil spill), and 2) catalysis. Oil emulsification involves understanding the action of surfactants on the oil-water mixture, which inherently involves self-assembly of structures resulting from this oil-water interface.

Dr. D. Van der Meer is Director of KSLA, and he was most interested in maintaining a balance of R&D efforts supporting the continuum of programs from basic to applied research, with ample efforts associated with the transition of ideas to products. About 3 percent of the company's R&D funding goes to outside universities. Another interesting point of view mentioned was the value of simulation research in guiding and working with experimentalists. This was not formerly the case, however clearly simulation is becoming an important ingredient in the full spectrum of R&D for the oil companies. Further aspects of this were discussed with the head of the Measurements and Computer Applications Group.

Shell Laboratories in Amsterdam supports modeling associated with new opportunities. These are divided into programs in 1) sensor physics, robotics, etc.; 2) computation and mathematics on parallel computers; 3) optimization techniques; and 4) process systems. The parallel computer at the laboratory, the 400-node "Transputer" with about 0.6 Gflops capability, is being replaced with an IBM SP-2 with 30 nodes and a peak rating of 6 Gflops. With the 400-node Transputer, typically 80 percent of peak performance is obtained with molecular dynamic simulations.

The principal problems on which simulation has become a very important component of R&D here is 1) fluid flow (principally cellular automata methods for modeling behavior in fluid-flow reactors), and 2) molecular dynamics and quantum mechanics, associated with oil emulsification and catalysis. Some recent success is found with modeling the crystallization of polymers through simulating molecule-molecule interactions through the glass transition temperature.

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## A6.2 Technical University of Delft

The Technical University of Delft is a science and technology university, with 12,000 students directed in technical studies. In addition, about 1000 graduate students pursue higher-level degrees with thesis study. Each undergraduate at Delft spends 1-1/2 years with about 60 percent of their time during this period pursuing research before obtaining their undergraduate degree.

Professor Radelaar is the senior professor associated with the Delft Institute for MicroElectronics and Submicron technology/Submicron (DIMES/S). This organization was created by merging members of the departments of physics and electrical engineering for the purpose of strengthening the total effort in mesoscale systems. Within DIMES/S, there are three major physics professors: 1) Radelaar (fabrication, materials, and transport physics); 2) Mooij (coherent quantum transport); 3) Wenckebach (optical physics).

DIMES/S is an institute supported by the Fundamenteel Onderzoek der Materie (FOM - Fundamental Research in Materials), which is the Dutch equivalent of the NSF in Applied Physics and materials, with an overall budget of about f100M/yr = \$56 M/yr (and an augmented special government grant for equipment of f30M/yr). Overall there are 20 permanent positions in DIMES/S along with 100 additional positions

involving technicians, students, postdocs, etc. The university supports the permanent positions and undergraduate student research; additional funding for graduate students and equipment comes from FOM. Some additional funding is from ESPRIT for research in areas such as single electronics. It is also pointed out that it is the only government funding agency in The Netherlands, as compared with the multiple funding agencies in the U.S.

Professor Radelaar's research group is studying microfabrication, materials fabrication and characterization, and mesoscopic effects. He has been involved with point contact measurements, hetero-epitaxial growth of aluminum on silicon (where there is a  $[4\text{-Al}] \times [3\text{-Si}]$  lattice match), SiGe 2-DEG behavior, electron beam lithography, and electron cyclotron etching. He is currently using electron beam lithography to fabricate 50 nm structures, and expects to be soon fabricating 20 nm structures for future efforts. He uses higher voltages to avoid proximity effects, which limit resolution under many conditions. Alternatively, he fabricates structures on thin silicon nitride films to get rid of some of the backscatter problems (standard technology). He also offered the opinion that industry doesn't like thin films or multi-layer resists because it introduces additional complexity in the fabrication process. An emphasis in the future will involve STM fabrication in a field-emission mode with chemical vapor deposition. He envisions obtaining one-nm resolution by using combinations of temperature, tunneling electrons, and optical effects in multiple stages for fabricating small structures. He sees the critical need for materials and lithography to work together to make advances here.

Professor Mooij has a group (within DIMES/S) consisting of four permanent scientists, 18 undergraduates, 13 graduate students, four postdocs, four "other" permanent positions, and 1 or 2 visitors. All permanent personnel are paid for by the university along with the costs of some "nuts and screws." FOM is the major supporter for the physics research and new equipment; ESPRIT funds two postdocs in single electronics. Professor Mooij is the coordinator for the ESPRIT program in single electronics. The four permanent scientists are 1) Dr. Harmans (semiconducting behavior, quantum dots and superconducting-semiconducting junctions); 2) Dr. Dekker (polymer chains, charge density waves); 3) Dr. Hadley (single electronics, and devices); and 4) Mooij (small tunnel junctions, and 2-D arrays).

This laboratory was the one that (with a cooperative effort involving Philips, Eindhoven) first measured the quantized conductance of a point contact. The group at Philips fabricated materials that had high mobilities, and the group at Delft did the lithography. Due consideration is also given to Prof. Pepper's group in Cambridge for measurement techniques developed there in about the same time frame. The Cambridge group introduced the depletion method of varying channel sizes, which was ultimately the method used to first observe the quantized conductance. The thesis by B. J. van Wees covered the first measurements on this subject, along with Henk van Houten at Philips. Dr. van Wees is now at the University of Groningen. It is clear that this group in Delft is responsible for graduating a large number of Ph.D.s who have become leading professors and researchers at other organizations.

The clean room facilities here are impressive, with two e-beam exposure instruments. The newest of these is a Leica Cambridge instrument (formerly Philips) which is under joint development with Leica at TU Delft. It has 100 kV capability and can produce a spot size of "a few nanometers." Lines of 10-12 nm width may be fabricated with this instrument at the present stage of its development. It has 16 bit addressability (15 of these effective for position/location, equivalent to 32,000 positions across the scan width) with an expected upgrade to 18 bits soon. Up to 10 6-inch wafers may be loaded into the machine, preprogrammed for exposure to patterns overnight, with the product available the next morning. This machine is used for educational/research purposes only.

In addition to the e-beam instruments, there is the usual array of etching, wet chemistry, optical exposure, etc. for a full complement of fabrication techniques. It was interesting to see the Scanning

Electron Microscope on which the high resolution lines were made that led to the discovery of the quantized conductance phenomenon. Nothing special, just a high-resolution SEM that had been modified for vector control of the beam.

Dr. Bart Geerligs occupies a permanent position in which he is responsible for setting up a new nanofabrication facility at DIMES/S (in addition to faculty and research responsibilities). This initiative is funded by special government support (through FOM) largely to introduce major hardware initiatives. This support amounts to f 8M (about \$4.5 M) over a 5 year period. This facility will include eight UHV chambers for 1) preparation of substrates and scanning probe tips; 2) XPS; 3) Al-CVD/STM for direct deposition of e-beam-enhanced pattern formation; 4) a cryostat for low temperature measurements; 5) an etching STM apparatus; 6) a chamber for manipulation of polymers; 7) a chamber for manipulation of clusters and atoms (single atom manipulation with proximal probes); and 8) focused electron and ion beams.

As for future directions in the group, some opinions were offered that areas such as quantized conductance of point contacts and single electronics are too popular with too many groups in the world today. Work with high temperature superconductors is being de-emphasized in this laboratory. There are ideas about alternative areas to pursue. These include subjects such as charge density waves, new regions of the electromagnetic spectrum, and conductance of organic polymeric molecules (oligomers).

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### A6.3 University of Groningen

The University of Groningen has about 6,000 students and is involved with general education in many disciplines. The University has a Materials Science Center and a Biomolecular Sciences and Biotechnology Institute. Drawing from faculty and students from both of these organizations is an organizational structure (interleaved) for nanostructures, headed by Professor T. M. Klapwijk. This group is involved with some efforts on the superconductor-semiconductor interface, ballistic systems, polymers, and STM, and consists of some well-established talent as well as a number of new faculty brought in to stimulate additional research in these fields.

Dr. Van Wees received his degree from the U. of Delft 5 years ago, and has one of several special fellowships from the Dutch National Academy of Science funding him to pursue research for a period of 5 years, at the end of which he will be given a full appointment at the University. He is following up on some semiconductor-superconductor interface programs at present.

Professor Ben Feringa in the Department of Organic and Molecular Inorganic Chemistry has found an important system for synthesizing materials which could be considered important for photochromic storage of information (molecular switching).

Professor G. T. Robillard is the Scientific Director of the Biomolecular Sciences and Biotechnology Institute. This Institute has been started within the last year at Groningen. It has direct support of f 10-15 M (\$5.6-8.4M) from the Ministry of Education for a 5 year period. At the conclusion it will be expected to have continuation support from granting agencies and industries. There are 35 academic staff and more than 300 people (including students) in this institute. The institute consists of programs in biomolecular protein engineering, surface science, polymer science, and macromolecular synthetic chemistry. After considerable soul-searching, the decision has been made to develop activities toward nano-engineering as opportunities arise to hire new faculty.



A comment was made that the biotechnology industry has a lobbying association in The Netherlands, which seems to be unique among the various industries in the country. An industrial-academic consortium in the country is allocating f 60-80M/year for biotechnology development.

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#### A6.4 University of Twente, Enschede

The University of Twente is a purely technical university with about 7,000 students. It operates somewhat in the same manner as the University of Delft, but is somewhat smaller. The MicroElectronics, Materials Engineering, Sensors, and Actuators (MESA) Institute is an institute formed about 5 years ago that contains many elements of nanoscience. It operates in a manner similar to that of DIMES at Delft, only it is somewhat smaller. Support for MESA comes from the university along with the Scheikunde Onderzoek der Materie (SOM - Chemistry Research in Materials) funded under government support.

Membership in this institute is of physicists, chemists, electrical engineers, and micromechanical engineers. Support for research is clearly through this umbrella institute, and some faculty are wondering if this will be the next organizational arrangement of the university, with the departments taking a back seat (if they even survive). The arrangement of research institutes at the universities in The Netherlands is an initiative of the national government. The consequences of this is to build areas of strength, allowing research efforts that do not fit into the pattern set up to either wither and die or to move elsewhere. Clearly most faculty are interacting cooperatively and are building within perceived strengths. This has stimulated considerable interdisciplinary cooperation for purposes involving sensors (chemical and biological mainly at this institute), information storage and logic, and optical systems for telecommunication.

MESA has 900 m<sup>2</sup> of clean room facilities, half of which is devoted to semiconductor research, and half of which is devoted to sensors and integrated optics. This division of resources has been instrumental in attracting members outside of solid state physics into research associated with nanostructures.

The Department of Chemical Technology at this university is the largest chemistry department in The Netherlands, and, in terms of numbers of Ph.D. graduates, ranks along with the 5th or 6th-largest institution in the U.S. with 45 Ph.D. graduates per year. Professor David Reinhoudt is a Professor of Organic Chemistry who has been working with the concepts and experimental implementation of "molecular recognition" for about 20 years. In this respect, he is one of the first researchers to recognize the importance of this field, and has been instrumental in introducing some innovative approaches to molecular recognition. He is the Section Editor of a Supramolecular Science and Technology section,

which is currently being introduced in the journal *Nanotechnology*. He has substantial responsibilities for coordinating the research within MESA and the government agencies as well as in European Headquarters in Brussels. Ultimate goals of his group include the fabrication of specific Ion-Selective Field Effect Transistors (ISFETs), new laser gain media, and new nonlinear optical materials.

Costs for the research program are supported by the university as well as by the sponsoring agencies. The example mentioned is that of organic chemistry, which has about 50 people (22 Ph.D. students). The university supports one professor, one associate professor, three senior research staff, two technicians, and three Ph.D. students. The remaining 19 Ph.D. students are supported at a rate of approximately f 400-500K/4 years (\$220-280K in 4 years). Student salaries are about f 40K/yr; the remaining expenses go to using equipment available and laboratory space, analyses, travel, etc). A definite propensity to think in terms of four-year grants was noted, as this is the length of time it takes for the degree to be granted.

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#### A6.5 Philips Research, Eindhoven

Philips Research is a large (2000 person) industrial research laboratory in downtown Eindhoven. It is clear that the research here is driven by industrial objectives. Nanoscience had a definite impetus when Henk van Houten at Philips jointly discovered quantized conductance with researchers in Delft. There is still some interest in nanoscience, but it is clear that research directions are to be tied in to those objectives that are consistent with the company objectives.

Discussions with Henk van Houten were useful in gaining some perspective in the research and technology areas of interest in his group. Likewise, discussions with Christian Schönenberger showed insight into those nanoscience areas of interest at the laboratory. Philips has considerable interest in telecommunications and memories (especially magnetic memories), thus research in areas such as lasers, soliton propagation, and light-emitting polymers have a good deal of emphasis. Some research continues in areas of nanostructures and thin films (especially magnetic thin films).

The laboratory has had strength and recognition in past nanoscience efforts in quantized conductance (seminal in this area) and thermopower measurements in nanostructures [349-350]. Room temperature

coulomb blockade measurements showing steps in the I-V curve were demonstrated here 3 years ago with a tunneling tip oriented directly over a metal cluster.

There is some feeling that areas of nanoscience which will continue to be of interest are more allied to areas of "nanotechnology." Areas of future emphasis include work with organic semiconductors (for possible use as alternatives to liquid crystal displays with an "all-plastic cathode ray tube"). One advantage that organic semiconductor materials offers is the possibility of fabricating circuits with silk screen printing techniques. Inexpensive production methods, of course, give market advantage. Large-scale electronics using synthetic metals also are of interest. Some feeling was expressed that if nanoscience is to have an impact industrially it will be in the area of lithography; it is, after all, the basis for fabrication of products (and profit) for industrial organizations.

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## **A7. SWEDEN**

### **A7.1 University of Lund, Lund**

The University of Lund, about 320 years old, is a full discipline university with about 30,000 students. The Physics Department conducts some research in nanoscience, and has eight "faculty:" 1) Elementary Particle Physics, 2) Heavy Ion Physics, 3) Applied Nuclear Physics, 4) Atomic Physics, 5) Atomic Spectroscopy, 6) Solid State Physics, 7) Synchrotron Physics, and 8) Combustion Physics. There is also a separate organizational element for theoretical physics, models for the nucleus, and solid state theory.

There are about 35 people (including predoctoral students) in Solid State Physics, of which about 25 are associated with a group headed by Professor Lars Samuelson. Prof. Samuelson's group includes subgroups in Lithography/AFM, Epitaxy/MOCVD/MBE/CBE, Spectroscopy, an Industrial coordinator, and an Industrial liaison. Sponsorship comes minimally from the university (salary of principal professor plus half of an associate) and principally from the Natural Sciences Research Council (NFR), the Research Council for Engineering Sciences (TFR), and the National Board for Industrial and Technological Development (NUTEK). A new thrust involving a consortium for nanoelectronics supports about half of future efforts in this laboratory. This consortium is funded by the NFR and NUTEK, and can be extended to a maximum of 10 years (anticipated for important programs such as those in the nanosciences). Ericsson, Inc. provides support and oversight to a number of technical programs in Sweden through board memberships; its mobile electronics is striving to introduce lower power (for increased mobility) and higher frequency devices.

An interesting sidelight, and one which may be a useful probe for some nanometer behavior, is the synchrotron at the U. of Lund. A new synchrotron is almost completed; it will have 20 ports (3 are presently functional) utilizing a 1.3 GeV beam. The high flux of X-rays emitted is envisioned for studies involving surface structure, which certainly contains nanostructures of many varieties.

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## A7.2 Chalmers University of Technology, Göteborg

Chalmers University of Technology is a technical institution with about 4000 students and 2000 full-time personnel at the university (half technical, half administrative or technician). There are about 100 professors, 100 lecturers, and 1000 predoctoral students. An additional 1000 students from the University of Gothenberg take courses at Chalmers University. The university budget of 1 B Krona (about \$100M) is divided into 2/3 research and 1/3 basic education. The principal part of research funding comes from external sources.

The Physics Department consists of subdivisions of 1) Applied Physics, 2) Microelectronics, 3) Nuclear Physics, with additional efforts in atomic physics and environmental physics. The traditional strength in the department is condensed matter physics, in particular, in electron spectroscopy. Angular photoemission originated in this university. A growing component of the university is that of Solid State Physics and Microelectronics. There are moves to combine these two disciplines, and a new building is being erected to house the expansion and this new organization.

The Chalmers Advanced MicroElectronics Laboratory (CAMEL) consists of various instruments, including lithography (a JOEL JBX-4DII installed in 1986 with a beam diameter of 8 nm and 16 bit positioning; it can handle 5" substrates), a scanning electron microscope (JOEL JSM-6301F field emission with 1.3 nm resolution, installed this year), two MBE machines, III-V processing, capability of fabricating Micro-ElectroMechanical Systems (MEMS), liquid crystal materials, and ion implantation. Clean room facilities consist of 50 m<sup>2</sup>. This is a center for fabrication of nanostructures to be utilized by other institutions in Sweden, although by far the majority (90 percent) of CAMEL is used by programs at Chalmers University.

Professor Tord Claesson is in the Applied (Solid State) Physics subdivision, and has been involved with superconducting tunneling for a number of years. One of the directions pursued with these devices is that of detectors for space observations at 100 to 350 GHz frequencies. The desire to extend instrumental capabilities to higher frequencies stimulates a thrust in smaller structures. Capabilities in fabricating semiconductor devices has developed here, which augments the flexibility involved with superconducting structures. This group consists of some 30 to 35 people, including six FTE from the Former Soviet Union (FSU). The FSU researchers typically spend three-month periods at Chalmers. Leonid Kuzmin, from Moscow State University, was associated with Chalmers University for 4-1/2 years and is now moving to Braunschweig, Germany. Support for programs totals approximately \$2 M/yr, with approximately 20 to 25 percent from the university. Other sponsors include the Natural Science Research Council (NSR), the Board for Industrial and Technical Development (NUTEK), the Research Council for Engineering Sciences (TFR), the Board of Heavy Industrial Development, European Community (ESPRIT) programs, the European Space Agency, the NORdic Program for Applied Superconductivity and a Materials Consortium. Some programs of an engineering nature are supported 50 percent by the government matching any industry support, an interesting way to leverage industrial interest in innovative ideas emerging from such research laboratories.

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## **A8. SWITZERLAND**

### **A8.1 IBM, Ruschlikon**

Dr. Heine Rohrer is, of course, one of the preeminent research scientists in the world today. As a Nobel Laureate in Physics for his co-discovery of scanning tunneling microscopy, his views and opinions are sought widely, particularly in the nanoscience and nanotechnology communities. It is clear that his contributions today consist of continual scientific oversight along with advice to numerous top-level groups and to scientists at IBM. His views about the scientific atmosphere that makes research most productive were fascinating to explore with him. It seemed to be the subject in today's scientific world that he was most anxious to discuss.

Dr. Rohrer was Head of the physics component of the IBM Zurich Research Laboratory that produced two Nobel Laureates in physics over the last decade (for high temperature superconductivity and scanning tunneling microscopy). His views about the research environment in a laboratory should hold considerable credibility.

IBM Zurich is 80 percent funded internally. A researcher has considerable freedom in deciding research directions, although some loss of this freedom of choice is being experienced now at IBM. The research laboratory has had a 20 percent reduction over the last several years, none of which has caused hardship separations. Universities today don't have this freedom of choice because proposals have to be written to compete with all other researchers, a process that is causing major difficulties for research in general. Every proposal justifies what the researcher is going to do, a process that limits the flexibility of choice necessary for innovative research.

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## A8.2 Paul Scherrer Institute, Zurich and Villigen

The Paul Scherrer Institute (PSI) is the largest Swiss-supported government laboratory with about 1200 people. The budget for the laboratory is approximately SFr 100M (\$75M) with an additional SFr 25M from specific contracts from various outside organizations. A little more than a third of the laboratory is now devoted to materials research, a change from previous emphasis which was almost entirely nuclear engineering and basic particle physics. It appears that the definition of the various research groups in PSI is under way after several acquisitions and a change in emphasis from largely nuclear effects to a much greater emphasis on materials.

In 1993, this institute established a group to work in nanotechnology. The group, headed by Dr. Jens Gobrecht, currently has 13 people. By the end of 3 years, it is expected to employ between 20 and 25 people. Incidentally, Dr. Gobrecht is the Secretary for the Swiss Society for Nanoscience, of which Dr. Rohrer is President. This Society provides for professional exchange of information.

The larger part of the laboratory is located in Villigen, Switzerland. A smaller part is located in Zurich, which is, in fact, the remaining research group of what used to be RCA research, acquired by G.E.,

and then sold to Switzerland. The Zurich component contributes strength in solid state physics, optics, and communications. This portion of PSI has many fabrication tools for semiconductor research, including III-V MBE, focused ion beams (with less than 50 nm resolution), and the usual processing tools to make semiconductor devices.

The nanotechnology group has four main areas of emphasis: 1) molecular; 2) devices (e.g., solar cell research); 3) new manufacturing methods (FIB, MBE, AFM); and 4) new analytical tools for sensing, etc.

One program involves an immunosensor in which a ferrocene molecule is found to interact with an antibody to act as a transducer. One component of the antibody binds to an insulator, and the second part to a comb-edge sensor that detects a change in redox potential with a ferrocene component near it.

Using the ability to fabricate such surface relief structures (discussed below), diffraction gratings have been used with silicon to diffract and trap light transmitted through the surface of a photocell. The light diffracts to a more horizontal direction, enhancing the interaction length between the incoming light and the semiconducting optical transducer. Experiments confirm that the optical thickness is enhanced in this manner by a factor of approximately eight. It is anticipated that the efficiency of solar cells may be enhanced considerably using this approach.

Additional capabilities and programs being introduced into this group include the LIGA process for fabricating small silicon structures (familiar to the microelectromechanical systems (MEMS) community), a defined growth of zeolite structures, along with new analytical and computational methods.

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### **A8.3 Eidgenoessische Technische Hochschule (ETH) Zurich (Swiss Federal Institute of Technology), Zurich**

The Eidgenoessische Technische Hochschule (ETH), Zurich is a technical university with approximately 11,000 students located in downtown Zurich. Two programs are being introduced that have components of nanoscience. One is in the area of chemical fabrication of nanostructures. François Diederich is an organic chemist who moved here two years ago from UCLA. His interests lie along the design of molecular systems that exhibit interesting and/or unusual properties due to conductivity, geometry, nonlinear coefficients, or other properties of interest. Several molecular systems are described below. His group is growing rapidly and currently contains 30 people, including 6 to 8 postdoctoral positions and two assistant professors. Steve Benner is able to fabricate interesting geometric structures from proteins containing modified base pair sequences.

The second effort is in the process of being formed, and is not yet funded. A number of faculty have joined together, with the stimulus of the Vice President for Research, Dr. Ralf Hütter. A program at the national level has been proposed by the name of Micro and Nanosystems (MINAST). If this program is successful (with good reason to hope for success at this stage), it will start on 1 January 1996. It will bring



together federal institutes and industry with a goal of 50 percent participation by industry. Some 90 companies currently wish to participate.

Some concern was expressed that the funds for this program could migrate to Brussels and be allocated by the EC. The "fighting spirit" was also introduced by those in the group inserting the challenge to go after it in Brussels if that is what happens to it. This is a microcosm of what seems to be happening in many places in Europe, with the centralization of research funds for EC oversight and "unification." As a general observation, I found many examples of scientists in Europe cooperating across country borders, considerably more than industry (comments heard repeatedly), with the country boundaries becoming almost as invisible as those between states of the U.S..

It was noted that a number of graduates from Swiss schools take postdoctoral positions in the U.S., however few funding mechanisms exist for encouraging graduates from U.S. schools to take postdoctoral positions in Switzerland, or in Europe in general. Some attention to this deficiency was requested. The cost of a postdoctoral position in Switzerland is approximately \$40-45K, including travel expenses. A second observation was made regarding the NSF centers in the U.S. From a perspective offered from Switzerland, these U.S. NSF centers have a good deal of in-breeding; it is difficult to start new efforts with additional people who are not already part of the "network."

Efforts are under way here in the general category of "supramolecular chemistry." These programs involve synthesizing large molecular structures that can perform such functions as binding (or "recognition") with specific molecules of interest. One program is under way to design molecular systems to recognize cholesterol. If cholesterol selectivity can be achieved, there are hopes of incorporating this in a resin for filtering blood.

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#### A8.4 University of Basel, Basel

Professor Güntherodt in the Physics Department at the University of Basel was one of the first researchers to begin using local probes in 1982, shortly after their discovery. His laboratory today has ten different home-built instruments and five commercial ones. Problems being investigated include surface reconstruction observations, frictional phenomena, magnetic force microscopy on superconducting materials, dynamic force microscopy on biological materials, the use of local probes as machining tools, and coulomb blockade phenomena. He has interests in several practical and industrial applications of these techniques [351, 352].

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## Appendix B

### PROCEDURAL/ORGANIZATIONAL OBSERVATIONS

#### B1. THE ORGANIZATION OF RESEARCH IN EUROPE

Information obtained about various funding sources and impressions about the organizational advantages and disadvantages are advantageous to consider. The perspective offered here is by far from complete, but rather, it offers a few salient points gathered from a limited yet fairly broad contact with a number of scientists in Europe. It should be considered as a contribution to the larger picture by combining such viewpoints with others gathered through a number of such experiences.

##### B1.1 Country-Wide Programs

Without doubt, a definite trend throughout all countries in Europe is that of creating a greater tie between university research and industrial interests. This is evident in the attitudes of researchers as well as some reorganized funding organizations and modified objectives in the funding agencies. This dominant theme is found throughout the research environment.

###### *B1.1.1 Government/Industry/Academic Cooperative Partnerships*

An interesting approach to program definition was mentioned during a conversation in Germany. The Bundes Ministerium für Forschung und Technologie (BMFT) initiated the program in 1985. This involved a group of researchers interacting for the purpose of examining ultrathin polymer layers, supported with 60M DM (about \$36M) over an eight-year period. The partners included BASF, Höchst, Bayer, Siemens (all four industrial), as well as academic researchers from Universities in Münster, Gottingen, and Mainz. The objectives of the program were to look in detail at this area of polymers and deduce the potential utility. Academic partners could work in industrial laboratories and vice versa. The industrial partners are now starting programs on their own (for example, Höchst has a program on membranes for gas separation, Bayer in biosensors, and BASF in surface modification). Academic partners have equipment from this program and are associating with other research programs sponsored by new consortia or industry. A significant plus for industrial partners was the improvement of existing products resulting from the collaborative efforts. Interest in the applications of scanning probe microscopy for the chemical industry is quite evident in the work done here [353].

###### *B1.1.2 Swiss Programs in Local Probes*

The Swiss Secretary of Education and Science called a number of researchers together last year to ask what the Swiss really had to offer. Arguments involving nanoscience were favorably heard because of the Swiss legacy for precision with small objects (Swiss watches being the notable example). Last year the Swiss Nanoscience Society was formed, but that is a society for interaction, not coordination.

There was finally a Swiss initiative in spatially resolved chemistry and physics of surfaces, selected in 1986, which started in 1987 and has produced about 100 Ph.D.s to this date. Even today, finding funds to continue some of these programs is coming up against solid entrenched programs in chemistry and the machine sciences which seem to be content with their current programs and techniques, unwilling to incorporate some of these new ideas into their programs. Biologists in Switzerland are comfortable using

an old and familiar tool, the electron microscope. They are reluctant to introduce the new and untried tool of local probes. There will probably be another new Swiss program involving nanostructures; Dr. Rohrer will be an advisor to this program.

### *B1.1.3 LINK: A Program to Stimulate Nanotechnology Transition*

A program designated as "LINK" has been in effect for several years in the United Kingdom. The purpose of LINK is to bridge the gap between science and the market place. LINK's basic objectives are to encourage collaborative research between industry and the research base in the UK to increase industrial competitiveness. Half of the program's funds are allocated by the government and half from industry. It is expected that these programs will stimulate industry to increase its own R & D investment. LINK's first programs were announced in 1958; nanotechnology was one of the 29 programs associated with that program of over £200M. Program duration is typically 3 to 6 years.

The nanotechnology program within LINK has 28 projects with a total funding level of £23.6M. A large number of the programs supported by this program are directed at precision machining and measurement of very precise components for metals and alloys (bearings, discs, gyroscopes), optical components, ceramics, sensors, actuators, vacuum microelectronic components, etc. Also included are damage-free semiconductor substrates, film/layers on an atomic scale, and the production/handling and characterization of ultrafine powders and biological materials.

## **B1.2 European-Wide Programs**

ESPRIT is the European Strategic Programme for Research and Development in Information Technology, one of the major subdivisions of the Commission of the European Communities (ECs), organized in Brussels. Its main thrust is that of advancing high performance microelectronics, computing, distributed processing, multimedia and display technology, and computer-integrated manufacturing. A number of programs in nanoelectronics are funded from ESPRIT with the proviso that the programs involve participants from more than one country within the European Community. The PHANTOMS program is funded by ESPRIT. A number of programs funded by ESPRIT are included in portions of this report. It is effectively providing stimulus for cooperative programs among the various EC countries.

## **B1.3 Interaction with Countries Outside of Europe**

A number of interactive programs with Japan were noted. For example, Dr. Nakazato is a scientist pursuing nanoelectronics in the Microelectronics Centre located at Cavendish Laboratory, Cambridge. He is supported by Hitachi of Japan. His group of approximately seven students and postdocs is looking at single electron phenomena and electronic devices associated with these small nanostructures.

## **B2. RESEARCH MANAGEMENT PERSPECTIVE**

A number of comments received related to the research atmosphere and the programs pursued now in comparison with those of earlier periods [354]. The atmosphere which we are creating for our researchers seems to be far less productive than that in the past. Whether this is a question of "the good old days" or a subject of serious debate among science leaders depends on perspectives which the reader brings to this. However it should seem clear to every reader that this subject is one which affects all of our lives, as researchers and as members of the future society. Quotes in this section are attributed to Dr. H. Rohrer.

"Don't coordinate the competition away." Coordinate when people work in a known area, but not when the area of investigation is unknown. An example worth mentioning is a scientific paper heard recently, in which a researcher reported good local probe techniques for observing DNA. The images

observed were "quite reasonable." Because of its importance, many researchers have observed DNA with varying degrees of success, but none with good definition of the DNA features. This has included people with various backgrounds and motivations. This is necessary for success in science. In Dr. Rohrer's view, the recent observation is quite reasonable relative to other attempts to make similar observations. It consists of observations 1) on mica, 2) at 0.1 picoamp current, and 3) at 57 percent humidity (to obtain one monolayer of water on the mica substrate). The number of attempts under other conditions must have involved many thousands of different conditions not comparable to these; who would have guessed that this set of conditions was the one to reach for? It was obtained through the hard work and unsuccessful attempts by many to have the one successful attempt.

"There are two classes of scientists: 1) those who do what they are paid to do, and 2) those who are paid for what they do." Those involved with "programs" fall in the first category. They belong to a program which is outlined to have boundaries and blinders on. The true path to scientific productivity is that of accepting high standards.

Semiconductor electronics is still being pursued with the same old set of principles. We need something different today. Maybe someday we will be able to combine the methods of local probes and semiconductor electronics. Molecular electronics today does not seem to offer that opportunity in any foreseen time scale.

We can learn how to understand the world through LPs. "LPs are a central tool to study the nanoworld." "Once we know how to do things, we will do them differently."

"Investment is the enemy of more investment." Once an investment is made in a piece of equipment, we are under scrutiny to make it work. "The larger the investment the more quantum leaps are required or expected."

The term "scientific research" is meaningful. The terms "basic" or "applied" are not. What one must keep in mind are 1) a basic principle and 2) a product.

The ultimate test of whether a direction is a good one or not is novelty. Novelty should be the major criterion directing the choice of research directions. "You don't find new paths if you look only around the corner of your house. We must learn to look over the hills." "The major issue to look for in research is to solve a problem, not just to use a technique."

After examining a number of points outlined above, one conclusion reached is that we may have generated many of these problems in our research environment as a consequence of too many scientists, all competing for the same funds.

### **B3. THE MOTIVATION THAT LEAD TO THE DISCOVERY OF STM**

STM was discovered because of problems that were motivated by technological limitations. Within IBM were a large number of programs (e.g., the Josephson Junction, magnetic bubbles, memories) that involved oxides that were not well-characterized. The research direction was set to understand what could be done to understand "thing" oxides and to characterize these materials at a smaller scale of inhomogeneities, since that seemed to be what was an uncontrolled characteristic of problems encountered in all of these programs. Such a program would never have been supported by NSF in the states, for example. This is one of the values an IBM or an NRL can bring to the R&D system.

#### B4. PERCEPTIONS ABOUT U.S. PROGRAMS AS VIEWED IN EUROPE

There are few new basic things coming out in the U.S. now. There are lots of thrusts, but few new developments. The reason for this is that people in the U.S. now have to prove themselves before they do something. This may not be much worse than the European system, but the changes that have taken place in the States to the present system are much larger than the changes that Europe has encountered.

In the U.S., there is a belief in competition. However this is a problem in the U.S. "The ultimate in competition is to have no competition." (Winners in the competitive process will drive all others out) There is a need for stimulus or challenge in research, but not competition. The challenge should come from within ourselves—we should set our own standards and work on a problem.

A definite preference was expressed for the U.S. system of keeping research groups small. The larger research groups in Europe (headed by a strong professor, a number of academic staff, and many researchers) do not represent an advantage; no - keep it the way the U.S. now has it.

However, there is a tendency in the U.S. to sell things too early. Two embryonic research efforts in the U.S. (one at NIST, the other at IBM) could have discovered STM first - they were on the right path. However the researchers at these two institutions did not get encouragement for the path they were taking. One of them spent too much time attempting to reach  $10^{-14}$  Torr and not enough time on the critical part of the experiment.

"American scientists are put too early to too high an expectation of pressure." "Too high an expectation guides you into doing things you can show in a short time." Too much competition is driving us into short-term thinking.

The U.S. pioneered the way at the micron level. That, along with the invention of the 2-DEG has the stamp of the U.S. on it. Europe has the discovery of the quantum Hall effect, Tunneling Microscopy, and Quantized Conductance. Another European contribution to this world is that of the physical understanding of polymers (Nobel Prize to de Gennes).

##### B4.1 Observations about the U.S., Europe, and Japan

The U.S. picked up on local probe techniques faster than did Europe or Japan. Several leading researchers in the field were into these processes in 1982 and 1983. In Japan, it was 1984 or 1985 before people started this kind of research. In Switzerland, people had many electron microscopes and were not interested in introducing a technique that was so different.

The sales of LPs from commercial companies were of interest to Dr. Rohrer. Recently he asked these companies where their sales are. He obtained the following statistics (1990 or 1991 data):

SOLD TO:	Academia	Industry	
Sales of local probe instruments	50%	50%	
SOLD TO COUNTRY:	U.S.	Europe	Japan
of all those for science purposes	50%	25%	25%
of all those that went to industry	25%	12%	62%

One observation consistent with these numbers is that the Japanese industry does what "garage companies" do in the U.S. The Japanese industry looks at anything new as a chance for something to grow.

They are fast at implementing things. Their industries recognize things that are new. Large industry spends too much of its time "girding their loins" against attacks by other industries.

## **B5. EMPLOYMENT OF SCIENTISTS**

Discussions held with a number of researchers about the employment situation in physics reflected a consistently difficult picture for physics graduates in Germany. There are currently 2500 recent graduates in physics (diploma and Ph.D.) who do not have jobs in physics. This represents a serious situation that is under considerable discussion at higher levels in the Physics Societies in Germany.

## **B6. ISSUES**

### **B6.1 Selection of Research Programs**

Some views related to the way research is accomplished in the states were offered. In the U.S., people may jump too quickly into new fields. Perhaps we have too many scientists and the field is too competitive since this is happening. There also exists a gap between research and industry in Europe as well as the states, but not in Japan. "What is needed is some vision from industry." However, industry holds its cards close because they are in a competitive position. Surprise was offered at the insulation of SEMATECH from interaction with outside sources of information. Also, scientists need to agree upon what is important to pursue.

A European program termed Joint European Submicron Silicon (JESSI) has allocated approximately \$500M/yr within the European electronics community (mostly industrial) for the development of SRAM/DRAM, chips, and advanced materials/lithographic methods. European lithographic capabilities are approaching 0.25  $\mu\text{m}$  and are expected to reach 0.18  $\mu\text{m}$  with optical techniques. An opinion was offered that the most expensive part of the fabrication operation for chips is in the "back end," where conducting leads and metallization must be made to control the chip. A difference with JESSI as compared with the American SEMATECH is that JESSI decided that there was no need to build special laboratories, that cooperating industry was to use their own laboratories. The funding for JESSI is now decreasing to a little less than \$420M/yr, and will end officially in 1996. A current major question of concern is what to do when this program ends.

Opinions seemed to back up those offered in other countries, that research in the U.S. has too great a tendency to be justified in terms of applications. It is overdone in the U.S., and that feeling is beginning to filter in to decisions in Europe. What is really needed is to make decisions about what is good research and to protect the technology-oriented research from this feeling that applications should drive the research. An example of current concern was offered: to justify research in STM as a lithographic tool for potential industrial production methods is extreme. It has very little capability for competition with other approaches due to the large number of pixels which must be written per second. Rather, it is a tool which should be studied in its own right, not justified because it might go into production.

Opinions were offered that 70 percent of the stepper market today is with Japanese technology and 30 percent is with European technology. ASM-Lithography near Eindhoven is claimed to be the third-largest stepper supplier in the world. The U.S. has not appeared to be very aggressive in the lithography market, although the most aggressive lithography techniques are first used for memories, and secondarily for logic circuit production. The U.S. could possibly have a chance to work with optical lithographic methods if the scanning technique were to be pushed and developed. This is true because the trend toward exposing larger wafer segments is difficult since the optics and all associated hardware gets very bulky. The scanning technique might be a way to circumvent some of these problems. Again, opinions suggested that the U.S. needs to push and sustain strategic directions to maintain a competitive position in this market.



Opinions were expressed at a number of laboratories that conduction through channels with a "split gate" and phenomena such as the coulomb blockade are reasonably well understood.

### **B6.2 Selling Nanotechnology "Properly"**

Some concern was expressed about the possibility of overselling the term "nanotechnology," which is considered to be an unfortunate name to some extent. The problems associated with overselling the virtues of low-dimensional structures were recalled. When the field did not live up to its promises it became difficult to sell any research in the field. The same could be true with nanotechnology. Some individuals professing the visionary aspects of the field could lead to problems for the field overall.

What is clear is that the scientific endeavors of nanoscience and the technological consequences involving nanotechnology represent a field of major opportunity. It should be represented with responsible enthusiasm and supported with measured growth where true opportunities are apparent.

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